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OPTIMUM PURIFICATION TECHNIQUES FOR THE REMOVAL OF CONTAMINANTS FROM LIQUID LITHIUM AND RUBIDIUM

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NOTICES

C

FOREWARD

ABSTRACT

Techniques of analysis and purification of rubidium and lithium are described. A method for analysis of oxygen in rubidium based on freezing point depression was developed. The technique has a sensitivity of 10 ppm O_2 with a precision of ± 10 ppm O_2.

Oxygen was removed from rubidium by stainless steel, zirconium and 50%Zr-50%Ti alloy. The oxygen equilibrium value of rubidium in contact with stainless steel or zirconium is < 10 ppm at 1400°F; with 50%Zr-50%Ti alloy the equilibrium value is < 10 ppm at 800°F.

Hot trapping is recommended for purification of rubidium. Cold trapping was shown to be ineffective in removing oxygen. With 10 psi overpressure of nitrogen above rubidium, no evidence of rubidium nitride formation was observed. Rubidium hydride did not form when hydrogen was bubbled through rubidium.

A suitable technique for analysis of oxygen in lithium was not developed during the course of the contract. However, the relative potential of a number of metals as getters was evaluated by an indirect method. Zirconium is recommended as a hot trapping material for lithium for removal of both oxygen and nitrogen. There was evidence that cold trapping would remove oxygen and nitrogen, also.

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I. INTRODUCTION

A. Purpose of the Study

The purpose of this study was to develop optimum puri-
fication techniques for the removal of contaminants from liquid
lithium and rubidium. The contaminants of interest were oxygen,
nitrogen, carbon and hydrogen. An integral part of this study
was to develop and/or refine analytical techniques capable of
detection of these contaminants to the 10 ppm level. The ob-
jective was to establish basic data on removal rates, efficiencies
and the like — no effort was made to determine design data for
operating systems.

B. Effect of Impurities on Corrosion

Historically, a significant amount of information evolved
on sodium technology from a concentrated effort in developing a
sodium cooled reactor for the nuclear submarine, Seawolf. During
the early stages of this development, little was known concerning
the effect of impurities in sodium. However, it quickly became
evident that impurities can have extreme deleterious effects on a
sodium cooled system.

First, in those systems where a differential temperature
exists, contaminants can precipitate in sections where the tempera-
ture is less than the saturation temperature for a given contami-
nant. Frequently, this cold section is a cooler or heat exchanger
where heat is removed as part of system operation. Generally,
the passages in these colder sections are small, as dicated by
heat transfer requirements, and any material which precipitates in
these small passages can lead to plugging.

Secondly, the presence of contaminants can result in corrosion of the structural material of the system. For example, a 5-fold increase in oxygen concentration in sodium from 10 to 50 ppm results in a 17-fold increase in mass transfer of iron from stainless steel. Problems can result from this increased rate of corrosion by (1) reducing the useful operating life of the system or (2) providing a source of material which can precipitate and cause plugging.

Data on the corrosive effects of impurities in rubidium are practically non-existant and little quantitative information is available with respect to lithium. Qualitatively, the presence of both oxygen and nitrogen in lithium causes a significant increase in corrosion rate; some investigators feel that the effect of nitrogen may be more severe than that of oxygen.

In summary then, it is recognized that alkali metals must be maintained in a high state of purity if system integrity and trouble free operation are expected. It follows that purification techniques must be devised and that those techniques must be applicable to removal of any of the impurities which might be present.

C. Potential Impurities

In determining the potential impurities, the source of these impurities should be reviewed. These sources include:

1. Contamination during manufacturing and processing.

   a. Impurities in raw materials.

   b. Atmospheric contamination during manufacturing, transferring and packaging.

   c. Surface film on containers.

2. Contamination during transfer to storage systems.

   a. Atmospheric contamination.

   b. Surface films on connecting plumbing and receivers.

3. Contamination during transfer to operational system.

    a. Atmospheric contamination.

    b. Surface film on connecting plumbing and system.

4. Contamination during system operation.

    a. Atmospheric contamination.

    b. Leakage of other fluids into system.

It can be said without qualification that the most likely source of contamination is the atmosphere. The contaminants in the atmosphere which will react with lithium and rubidium are primarily.

1. O_2

2. CO_2

3. H_2O

4. Organic vapors

In addition to these, nitrogen can react with lithium. Some of the resultant contaminants which can be expected are:

1. Rb_xO_y	4. $RbOH$	7. LiH	10. Li_2C_2
2. RbH	5. C	8. Li_2CO_3	11. Li_3N
3. Rb_2CO_3	6. Li_2O	9. $LiOH$	

Most of these contaminants can be introduced during manufacture and transfer, from raw materials and surface films (including organic solvents which are not properly removed from metal surfaces), water vapor and absorbed gases. It is obvious then that the contaminants which will be encountered are primarily compounds containing oxygen, nitrogen, hydrogen and carbon.

D. Methods of Contaminant Removal

Methods which have been employed in purifying other alkali metals, particularly sodium are:

1. Filtration

2. Cold trapping

3. Hot trapping

4. Vacuum distillation

Filtration and vacuum distillation are useful primarily for pre-charging cleanup before or during introduction of an alkali metal into a system. Cold trapping and hot trapping have been used effectively during precharge cleanup, and for continuous purification during system operation.

Filtration is based on the temperature dependent solubilities of the contaminants. In practice, the alkali metal is heated just above the melting point (mp + 50°F) and is forced through a porous stainless steel filter. These filters are available with pore sizes down to 5 μ. Glass-wool and glass-fritted filters have also been used, but their use is not recommended because of the possible introduction of contaminants such as sodium, silicon, boron and oxygen. With filtration, the minimum level to which impurities can be reduced is that level which corresponds to the equilibrium saturation value at the temperature at which filtering is being conducted. With sodium, this corresponds to 20-30 ppm oxygen (oxygen saturation value at 250°F). It had been expected that the solubility of oxygen in rubidium at the melting point could be high so filtration should not be a feasible method for the removal of oxygen from rubidium. The solubility of oxygen[1] in lithium at 480°F is in the neighborhood of 100 ppm and this would represent the minimum level to which oxygen in lithium could be reduced by filtration. The solubility of nitrogen in lithium has been reported as ~1300 ppm at 480°F; filtration would be expected to be ineffective in removing nitrogen if the solubility value is correct.

Cold trapping is also based on the temperature dependent solubility of contaminants. Two types of cold traps are commonly in use - forced circulation and natural diffusion cold traps. A forced circulation cold trap is in essence a filter since the metal is cooled prior to entry to the cold trap where it is forced through a wire mesh bed which serves to remove

precipitated particles. A natural diffusion cold trap is in essence a cold sink attached to some section of the system and is maintained near or below the melting point of the metal. Oxide diffuses from the hot system and precipitates at the solid metal-liquid metal interface. Ultimate purity which can be attained with these devices corresponds to the equilibrium solubility at the temperature at which the device is maintained.

Hot trapping is based on chemical reactions of the contaminants with a reactive metal such as zirconium, titanium, uranium or thorium. The primary requisite of the hot trapping material is that the getter metal compound be more thermo-dynamically stable than the alkali metal compound. Other desirable characteristics of the material include formation of a compound which does not spall from the surface, rapid diffusion of the contaminant into the matrix of the material and low solubility of material and/or compound in the alkali metal. The lower limit to which impurities can be removed should be essentially unlimited, although there is a finite equilibrium which is controlled by the contaminant concentrations in the alkali metal and getter, temperature and other impurities. Oxygen concentration in potassium has been reduced to ~ 5 ppm through the use of zirconium.

Free energy of formation can be used as an indicator of the feasibility of a material as a getter. Table 1 lists some of the thermodynamic data for compounds which are most likely to be found in lithium and rubidium along with candidates as gettering materials. The available data are limited, but thermo-dynamic properties indicate that calcium, thorium, yttrium and beryllium might be used as getters for removal of oxygen from lithium. In addition to these metals, hafnium, uranium, zirconium, titanium, chromium and iron should be capable of reducing rubidium oxide. Similar analogies can be made with respect to carbides and nitrides.

Vacuum distillation can be used to remove certain impurities from alkali metals. The efficiency of the process as a purification method depends upon the specific alkali metal being purified and the impurities which are present. With lithium, other alkali metals, heavy metals and oxygen should be removed by distillation. The other alkali metals would be distilled during the early part of a batch distillation; heavy metals and oxygen would remain in the still pot. Nitrogen might be trans-ferred during distillation. Because of the corrosive nature of lithium and its associated contaminants and its high boiling point, vacuum distillation does not appear to be a particularly attractive method of purification.

TABLE 1 - THERMODYNAMIC PROPERTIES OF SELECTED METAL COMPOUNDS[1]

Oxides	$-\Delta F_{800°K}$ (Kcal/g-atom O)	Carbides	$-\Delta F_{800°K}$ (Kcal/g-atom C)	Nitrides	$-\Delta F_{800°K}$ (Kcal/g-atom N)
CaO	132	ZrC	42.2	UN	66.4
ThO$_2$	128	TiC	41.5	ZrN	63.6
Rare Earth Oxide	125-130	ThC$_2$	27.0	TiN	62.0
Y$_2$O$_3$	125	UC	26.8	Th$_3$N$_4$	59.7
BeO	123	YC	(2)	Be$_3$N$_2$	50.6
Li$_2$O	117	Li$_2$C$_2$	6.1	YN	42.0
HfO$_2$	114	Rb$_x$C$_y$	(3)	Li$_3$N	20.1
UO$_2$	112				
ZrO$_2$	112				
TiO$_2$	95				
Cr$_2$O$_3$	72				
FeO	50				
Rb$_2$O	34				

(1) Excerpts from Pratt and Whitney Technical Information Memorandum, TIM 651.

(2) No value given.

(3) No data.

In the case of rubidium, the heavy metals and the other alkali metals, except cesium, can be effectively removed by vacuum distillation. Rubidium oxide is one of the less stable alkali metal oxides and it is possible that oxygen would be transferred during distillation. In general, it is felt that vacuum distillation is acceptable for purification of small quantities of the alkali metals. However, for purification of large quantities of alkali metals, vacuum distillation is not particularly attractive because of difficulties in system design and operation.

E. Analytical Procedures

One of the major problems in this study was the development of suitable analytical procedures. It was recognized before the study was undertaken that the methods of determination of oxygen in lithium and rubidium were essentially non-existant. Neutron activation analysis had been used for analysis of oxygen in lithium down to ~ 100 ppm level. The amalgamation method had been modified for oxygen in lithium but the precision and reproducibility was poor. No information was available on the analysis of oxygen in rubidium.

Because the amalgamation technique has been used successfully at MSAR for the analysis of oxygen in sodium and potassium, the initial approach was to modify and adapt the amalgamation procedure to the analysis of oxygen in rubidium and lithium. These efforts ultimately proved fruitless. However, an alternate method was devised for the analysis of oxygen in rubidium.

No development work was required for the analysis of nitrogen and hydrogen in the alkali metals. A modified Kjehdahl method followed by measurement with Nessler Reagent is used for nitrogen and has a sensitivity of 2 ppm. Hydrogen is measured by the isotopic dilution method with a sensitivity of 2 ppm; this required some modification for the analysis of hydrogen in lithium.

Analysis of carbon in alkali metals is presently in a state of flux. Sensitivity to ± 5 ppm is attained at MSAR for standards, but analyses of replicate alkali metal samples do not reflect this precision. Much of the carbon problem is attributed to sampling techniques along with maintenance of a homogeneous system both before and after sampling. The method used in this study included dissolution of the metal with water at $0°C$, conversion of the caustic solution to the chloride, evaporation to dryness and combustion of the dry salt in a prepurified oxygen atmosphere.

Analytical procedures are discussed in detail in the Appendixes.

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II. EXPERIMENTAL APPARATUS

A. Introduction

A photograph showing the panel board and some of the purification vessels is shown in Figure 1. The complete system included 2 rubidium hot traps, 2 lithium hot traps, a rubidium cold trap and a lithium cold trap. Associated equipment included temperature controls, ammeters, transformers and the like. The inert gas purification system can also be seen in the photograph. Table 2 shows the impurity levels indicated by the suppliers of alkali metals.

B. Rubidium Hot Trap

A schematic diagram of the rubidium hot trap is shown in Figure 2. The hot trapping vessel was constructed of 3 in. Schedule 80 Type 316 stainless steel pipe. It was sized to fit an 1800 watt Kanthal tube furnace with a 10-in. heat zone and designed for temperatures to 1600°F. A 240-32 volt transformer and a 9 amp powerstat controlled the electrical input to the furnace. Since heat transfer characteristics were difficult to predict with mixtures of argon and rubidium vapors, a cooling coil was provided to maintain temperatures below 700°F at the gate valve and a dual valve arrangement was provided to protect the ball valve from attack by rubidium vapor.

A thermocouple inserted in a thermowell which extended below the liquid surface was connected to a West temperature controller which maintained the desired temperatures. A drain line extended to the bottom of the unit to enable draining of the unit while in the furnace. Each system contained $\sim$1360 grams of rubidium.

Provision was made to insert getter material in a wire basket below the liquid metal surface. A corrosion tab of stainless steel was attached to the stainless steel rods which held the basket. The getter basket was attached to the top flange and maintained in the hot trap during the experiment.

A freezing point apparatus was constructed and installed on the hot trap. A detailed description and explanation of its operations is given in Appendix A.
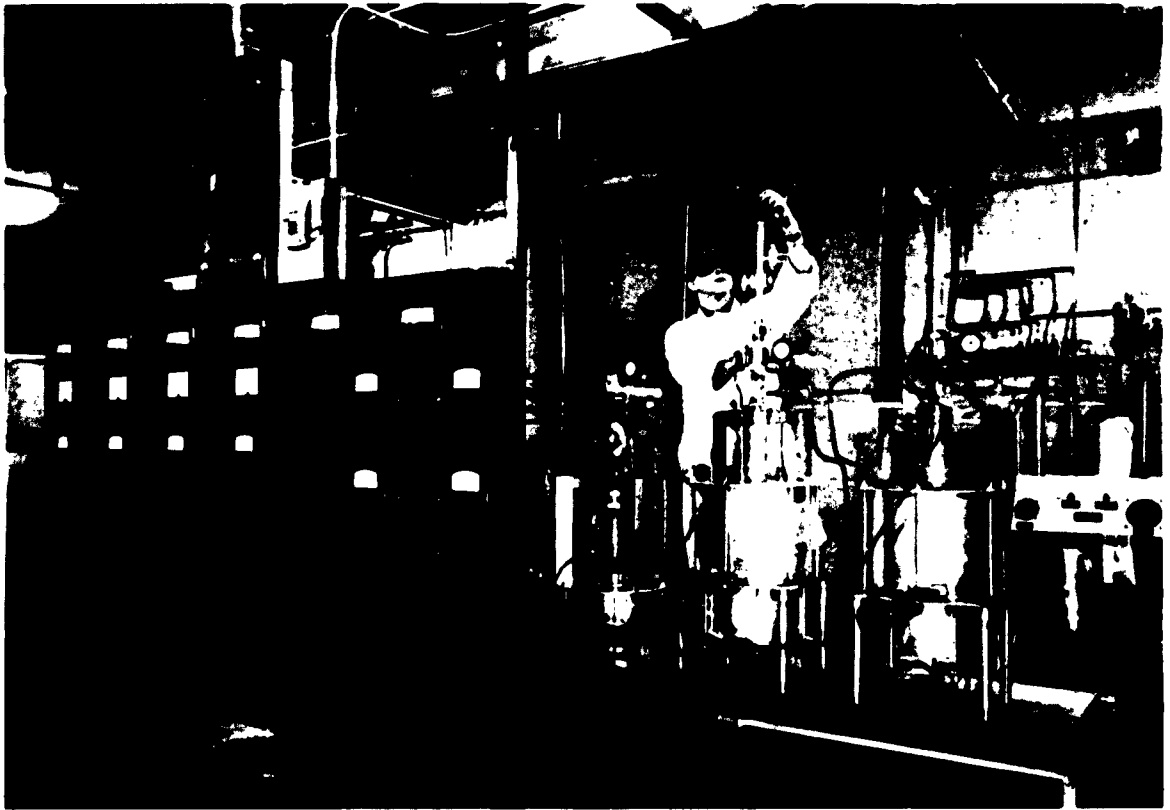
FIG 1 - PURIFICATION UNIT

TABLE 2 - SUPPLIERS ANALYSIS OF Li AND Rb

Element	Lithium (ppm)[1]	Rubidium (ppm)[2]
Na	50	30
K	75	50
Cl	50	--
N	40	--
Ca	10*	--
Fe	10*	5*
Ni	10*	5*
Cu	10*	5*
Al	10*	5
Si	10*	10*
Co	10*	5*
Cu	10*	2*
B	--	5*
Mn	--	1*
Mg	--	2*
Sn	--	5*
Pb	--	5*
Ti	--	5*
Mo	--	5*
V	--	5*
Be	--	1*
Ag	--	2*
Cs	--	1000 ± 500

* Signifies less than

1. Foote Mineral Corp.

2. MSA Research Corp.

FIG 2 - RUBIDIUM HOT TRAP

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C. Lithium Hot Trap

A schematic diagram of the lithium hot traps is shown in Figure 3. The low vapor pressure at elevated temperature (1.95 psia at 2000°F) enabled the design of a less complex unit not requiring a dual valve arrangement. The 2 vessels were constructed from 3 in. Schedule 40 Type 316 stainless steel. A 1-1/2 in. ball valve was attached to the flange which contained a stainless steel O-ring seal. A cover gas connection was situated just above the flange on the 2-in. pipe connecting the 1-1/2 in. ball valve to the flange. Temperature was maintained at $<200°F$ at the ball valve.

Each unit contained thermocouples necessary to control the temperature of the lithium, and to monitor vessel surface temperatures. The hot traps were heated in an 1100 watt Kanthal tube furnace with a 10-in. heat zone. The hot trap was filled to about 1 in. below the top of the furnace heat zone with 680 grams of lithium.

D. Lithium and Rubidium Cold Traps

A schematic diagram of the cold traps is shown in Figure 4. These vessels were made of Schedule 40 Type 304 stainless steel. A 1-1/2 in. stainless steel ball valve was used on each unit for sampling, filling and draining. The body of the cold trap was 3 in. pipe and the cold leg was 1 in. pipe. Two Kanthal tube furnaces were used to heat the body and upper portion of the cold leg. The body temperature was maintained with an 1800 watt Kanthal tube furnace having a 10-in. heat zone and the upper part of the leg was heated with a smaller Kanthal tube furnace. The lower portion of the cold leg was heated with nichrome heating wire which was controlled with a rheostat. A length of 1/4 in. stainless steel tubing was wrapped around the lower portion of the cold leg to provide cooling during cold trapping operations.

Temperatures were controlled manually and monitored with a 1/4 in. chromel-alumel thermocouple 20 in. long inserted in the body thermowell. External thermocouples were attached along the lower portion of the cold leg and a 1/16 in. Ceramo insulated chromel-alumel thermocouple was inserted in a thermowell in the cold leg to permit manual control of the lower heater. Heating of these units was manually controlled using a 9-amp powerstat and a 240-32-volt transformer. Each furnace had a separate control for the body and cold leg elements. The units operated satisfactorily, allowing isothermal operation up to about 600°F, and cold trapping operations with the body at 1000°F and the cold leg below 200°F.

FIG 3 - LITHIUM HOT TRAP

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FIG 4 – LITHIUM AND RUBIDIUM COLD TRAP

NOTES:

All Pipes Must Be Aligned

MS Test & x-Ray TC Wells

MS Test Assembly

Leave Threads Clean For Seal Welding

K-2263

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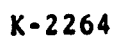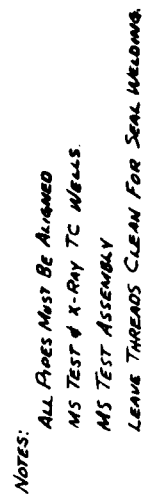
An inert gas purification system (MSAR Model 15H) was used to purify the argon cover gas. The system will remove water vapor and oxygen to ~ 0.5 ppm by bubbling through 600°F NaK; water vapor and oxygen in tank argon can range from 10-20 ppm. A zirconium hot trap for removal of nitrogen is also a part of the system. The purified gas was used for both system cover gas and sampling cover gas.

The rubidium cold trap was modified by the addition of a freezing point determination apparatus which is shown in Figure 5. A description of this apparatus and an explanation of its operation is given in Appendix A.

III. EXPERIMENTAL PROGRAM

A. Development of Analytical Techniques

1. Oxygen in Lithium - Before any experimental efforts on the removal of contaminants from lithium were undertaken, it was necessary to establish suitable analytical techniques. The analysis of nitrogen and carbon offered no problems, but a suitable method for the analysis of oxygen was not available. Adaptation of the isotopic dilution method for hydrogen in lithium was required. Hoffman[2] had used the neutron activation method to develop an oxygen in lithium solubility curve. At 480°F where the average solubility appeared to be ~ 100 ppm, the values varied from 58 to 121 ppm. With an average oxygen content of 650 ppm, the values varied from 477 to 766 ppm. It was felt that precision required for this purification study should be at least $\pm$ 10 ppm with a lower limit of detection of 10 ppm. This being the case, no further consideration was given to the neutron activation analysis method. Other methods, including the amalgamation technique, butyl bromide and methanol method did not appear to offer much hope either.

In light of the fact that the amalgamation procedure is generally accepted as a reliable method with a sensitivity of 5 $\pm$ 5 ppm oxygen in sodium and 10 $\pm$ 5 ppm oxygen in potassium, it was decided that an attempt would be made to adapt the method to the analysis of oxygen in lithium. In reviewing some of the work on lithium oxide analysis by amalgamation, it was found that one of the major problems was the interaction of lithium and/or lithium amalgam with glass. Modification of the procedure to

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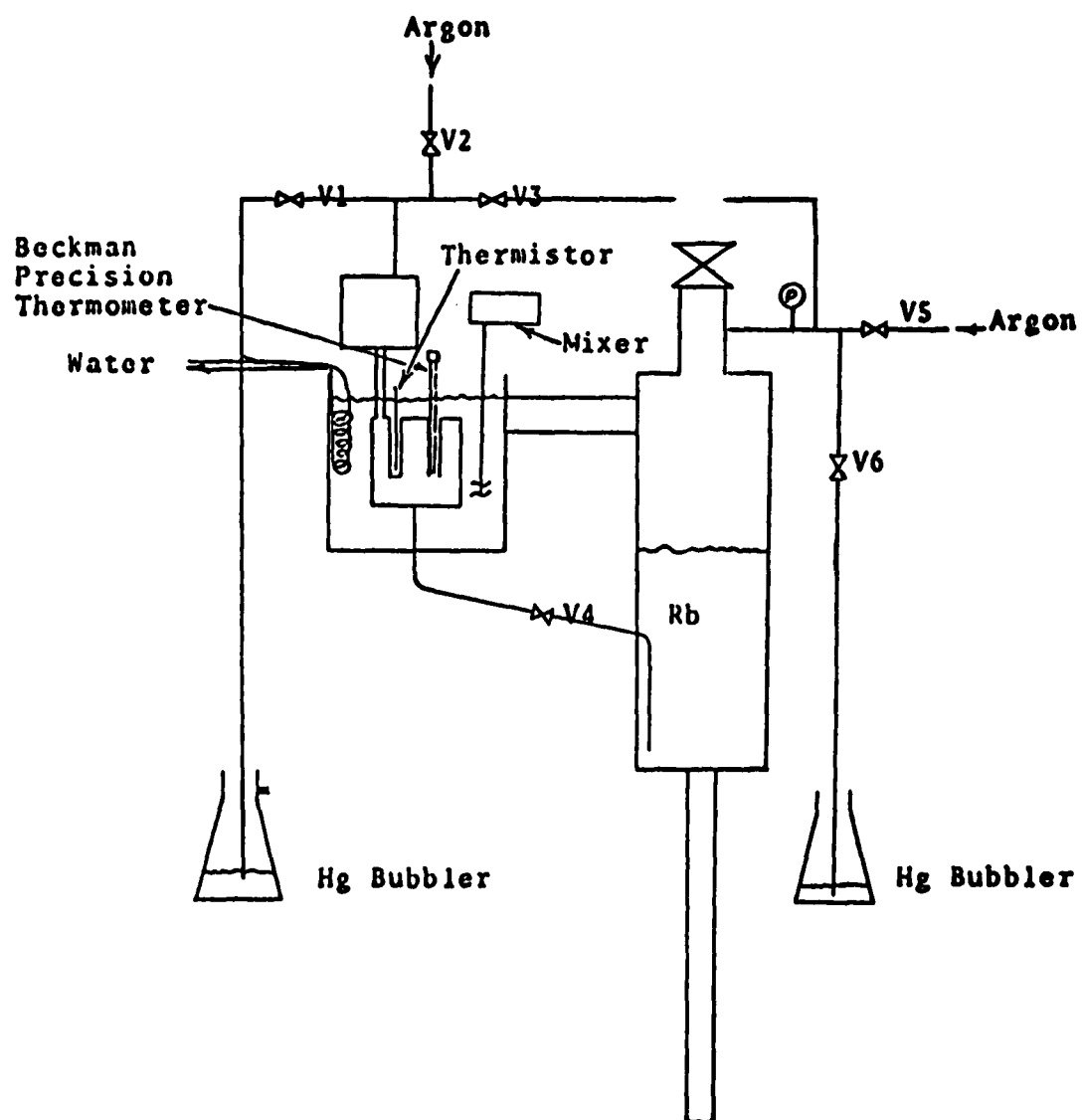
FIG 5 -FREEZING POINT APPARATUS FOR RUBIDIUM COLD TRAP

minimize or eliminate glass attack was the initial experimental phase of this program. To expedite the analytical development phase of the program, a special lithium vessel capable of 1000°F operation was fabricated.

High purity lithium was purchased from Foote Mineral Corporation; analysis supplied by the manufacturer is shown in Table 2. A portion of this material was charged to the lithium vessel through a micrometallic filter; during charging the lithium was maintained at $\sim$ 50°F above the melting point to minimize transfer of oxygen, nitrogen and other impurities to the vessel. The vessel was heated to 1000°F and samples were extracted for analysis.

The standard method of extracting dip samples from high temperature alkali metal systems is described in Appendix B. In essence, the sample is dipped from the melt in a nickel bucket with a capacity of 0.5 to 1 gram. The sample is extracted through a 1-1/2-in, valve into an inert cover gas apparatus. After cooling, the sample is transferred, still under inert gas, to an amalgamation chamber. The standard method of amalgamation is also described in Appendix B.

The first sample extracted from the special lithium vessel was placed in an amalgamation chamber and mercury was added. The sample required 3 days at room temperature with occasional mixing for complete amalgamation. The results of the completed analysis was 1213 ppm oxygen.

In the next analysis, heat was applied to the chamber by means of a heating mantle while the sample bucket of lithium was held above the mercury surface in an inverted position. When the temperature reached the melting point of lithium, the lithium was dropped into the hot mercury. The resulting exothermic amalgamation severely etched the amalgamation chamber.

By keeping the sample beneath the mercury surface during the amalgamation of the next sample, glass attack was localized at the bucket site and splashing of hot amalgam was reduced considerably.

Protection of the glass wall in subsequent analyses was provided by placing a stainless steel open-end cylinder (fabricated from 7-mil sheet) in the chamber. The mercury level was maintained just above the top of the cylinder. The sample bucket was held in an inverted position just beneath the mercury with a magnet. It was hoped that the hot amalgam would in this fashion be ejected against the stainless steel cylinder and that glass attack would be eliminated.

At this stage in the modification of the amalgamation method, it was felt the major difficulty of obtaining a rapid and complete amalgamation of the sample had been eliminated. To verify this, a standard procedure was followed for a series of analyses. (At this time, construction of the test vessels had been completed and the samples were extracted from the lithium cold trap #5 and lithium hot trap #1). The following method was followed for this series of samples:

The stainless steel shield was placed in the amalgamation chamber and the sample transferred to the chamber according to the standard sampling procedure (Appendix B). The sample bucket was positioned with a magnet so that the top of the sample bucket faced down and against the shield about 1 in. from the shield bottom. After mercury was added to a level just above the shield, heat was applied and the chamber surface was heated to 225°-230°C in fifteen minutes. If there was no sign of a reaction during the heating period, the temperature was held at 225°C for 15 to 20 minutes. This usually was sufficient for complete amalgamation of the sample. The heating mantle was removed immediately and the hot lithium amalgam was mixed slowly until the amalgam cooled to ~50°C. The analysis was then completed according to the standard amalgamation procedure.

Some of the amalgamations would take place rapidly as the temperature approached 200°C; others would amalgamate with no apparent reaction. Some of the reactions were sufficiently violent to eject amalgam or hot molten lithium on the glass wall in spite of the shield; this invariably gave a high oxygen result. Glass attack from contact with the hot amalgam resulted in a brown-black mark that could not be completely removed with successive mercury extractions but would react with the water during the oxide dissolution step. The chambers were etched permanently which indicated reaction with the glass.

A total of 36 samples were analyzed by the above method and of that number 18 resulted in definite glass attack of the chamber. Table 3 shows the results of samples from the lithium cold trap and Table 4 shows the results of samples from the lithium hot trap. The first two samples from the lithium cold trap showed 4480 and 3258 ppm oxygen. An electrical failure caused the cold leg to cool to 300°F for 12-13 hours. Samples

TABLE 3 - RESULTS OF OXYGEN ANALYSIS IN LITHIUM COLD TRAP #5

Sample No.	Date	Sample Weight (gm)	Control Temperature (°F)	Cold Leg Temperature (°F)	Oxygen Content (ppm)	Remarks
5	4-22-63	0.1526	1020	1080	4480	
11	4-25-63	0.2296	1020	1250	3258	
						Vessel cooled down 12-13 hours. Reheated to temperature.
15	4-26-63	0.3492	1000	1100	515	
16	4-29-63	0.1827	1000	1100	599	
18	4-30-63	0.3048	1000	1080	803	Bucket floated to surface and lithium etched glass.
20	5-1-63	0.280	1000	1090	603	
21	5-2-63	0.1790	1000	1090	550	
23	5-3-63	0.2500	1000	1090	295	
26	5-6-63	0.2930	1000	1080	423	
	5-6-63					Start cold trap.
27	5-7-63	0.390	1000	965	389	Glass etched.
31	5-8-63	0.354	1000	500	341	
34	5-9-63	0.473	1040	350	406	Difficult amalgamation.
35	5-9-63	0.250	1020	345	242	
37	5-10-63	0.500	1040	345	367	Glass etched.
39	5-11-63	0.471	1050	355	447	Glass etched.
41	5-13-63	0.263	1025	345	323	
45	5-15-63	0.270	1040	345	296	
47	5-17-63	0.350	1040	340	231	
52	5-21-63	0.830	1020	340	273	Glass etched.
65	6-3-63	0.742	1005	340	450	
69	6-6-63	0.212	1000	340	426	
81[1]	6-17-63	-----	1000	340	---	Glass etched.
84[1]	6-19-63	-----	1010	335	---	Glass etched.
85	6-19-63	0.680	1005	345	664	Difficult amalgamation.
86	6-20-63	0.359	1020	345	312	
90[1]	6-21-63	-----	1000	340	---	Glass etched.
91[1]	6-24-63	-----	1010	345	---	Glass etched.
93	6-24-63	0.306	970	340	264	
95[1]	6-26-63	-----	1005	340	---	Glass etched.

[1] Analysis not completed.

TABLE 4 - OXYGEN RESULTS ON LITHIUM HOT TRAP #1

Sample No.	Date	Sample Weight (g)	Control Temp. (°F)	Oxygen (ppm)	Remarks
54	5/22/63	0.203	1000	457	Glass etched.
56	5/23/63	0.600	1000	405	Glass etched.
57	5/24/63	0.511	990	- -	Analysis not completed.
58	5/24/63	- -	- -	- -	Analysis not completed.
59	5/25/63	0.700	995	891	Difficult amalgamation.
61	5/27/63	0.613	1000	384	
62	5/27/63	- -	990	- -	Analysis not completed.

taken after the leg was reheated, as seen in Table 3, were considerably lower in oxide content although the cold trap was returned to a temperature 80° to 100°F above the control temperature of 1000°F for 5 hours before the sampling was resumed. This suggests that cold trapping might be an effective means of removing oxygen from lithium. Averages of the samples that did not show etching and glass attack showed 497 ppm oxygen with an average deviation of ± 92 ppm oxygen for the lithium cold trap with the system at isothermal conditions. The results of the samples run after cold trapping was initiated gave an average of 318 ppm oxygen with an average deviation of ± 61 ppm oxygen. Although the method of analysis was of questionable reliability at this state of development, the results indicated that cold trapping was feasible. No quantitative conclusions could be made because of inadequacies of the analytical method.

The effects of amalgamation rates and temperatures were evaluated. A lower heating rate was used at the start and increased until the amalgamation was completed. This was done by heating at 150°C for 1/2 hour; if the amalgamation was initiated the temperature was increased to 200°-220°C for 1 to 1-1/2 hours. The progress of amalgamation was checked by raising the bucket from the mercury with a magnet and observing the sample level in the bucket at the end of each heating period. Twelve samples were run in this manner and 5 were contaminated as a result of the violent amalgamation that etched the chamber. Several of these reactions occurred when the bucket was raised above the mercury for inspection after the 200°C heating period. One such reaction at the mercury surface broke the amalgamation chamber. The average oxygen content of the remaining seven samples was 210 ppm oxygen with standard deviation of ± 58 ppm oxygen. The sample attrition rate at the lower amalgamation temperature remained the same as the other techniques at ~50%. The oxygen content appeared to be lower (210 ppm) but the precision of ± 58 ppm oxygen was not significantly improved over the rapid heating method (± 61 ppm).

Two experiments were performed at room temperature using ultrasonics to increase the amalgamation rate. A chamber containing a 0.3 gram sample was submerged in an ultrasonic tank. After 1 hour, about half of the sample was amalgamated. A dark grey powder formed on the surface of the mercury as the sample amalgamated. Room temperature amalgamation of the 0.3 gram sample required about 3 hours but a 0.9 gram sample did not amalgamate completely in 48 hours. In the analysis of the amalgamated sample successive mercury extractions did not flush out the powder and a high result (953 ppm) was obtained. Since the fine powder could not be extracted with successive mercury washes, this modification was discontinued.

The degree of reaction of lithium amalgam with the glass chamber wall was evaluated at three temperatures - 25°, 150° and 230°C. The tests were made by transferring lithium amalgam from the first amalgamation chamber to a second chamber. The oxide present in the original sample and formed by reaction with the walls during amalgamation was left in the original chamber. The two amalgamation chambers were connected at the drain stopcocks by a short piece of glass tubing. The tubing was attached to the chambers by 12/5 standard ball joints. The second chamber was evacuated, flamed and flushed with argon following the same procedure used during normal sampling. The amalgam was forced from the first chamber to the second with argon pressure, a small residue of amalgam was maintained in the first chamber to hold back any oxide. If the amalgam did not react with the glass, no oxide would be found in the second chamber. Three experiments were performed with the following results:

Sample No.	Weight (g)	Temperature of Chamber (°C)	Time at Temperature (hr)	Oxygen Found (μg)
1	0.218	25	1	17
2	0.403	150	1	42
3	0.216	230	1-1/2	79

The results show an increase of apparent oxygen with temperature indicating that the glass walls are attacked by the amalgam. The weight of oxygen found in those samples analyzed at lower temperatures was plotted against the sample weights. Extrapolation to zero weight gave a blank of 55 μg oxygen (Figure 6). Not all the points fall on a straight line therefore the oxygen level did not remain constant in the lithium vessel (cold trap #5) during prolonged cold trapping or the effect of glass attack is variable. Since the localized temperatures reached during the exothermic amalgamation are not known, and it has been shown that glass attack is temperature dependent, a constant blank could not be subtracted from the oxygen found in any one analysis. Work with the glass chamber was discontinued and several metal chambers were tested.

Figure 7 shows the metal amalgamation chambers which were tested. Samples were transferred to the metal chambers from the sampling head by the standard method. The glass adapter
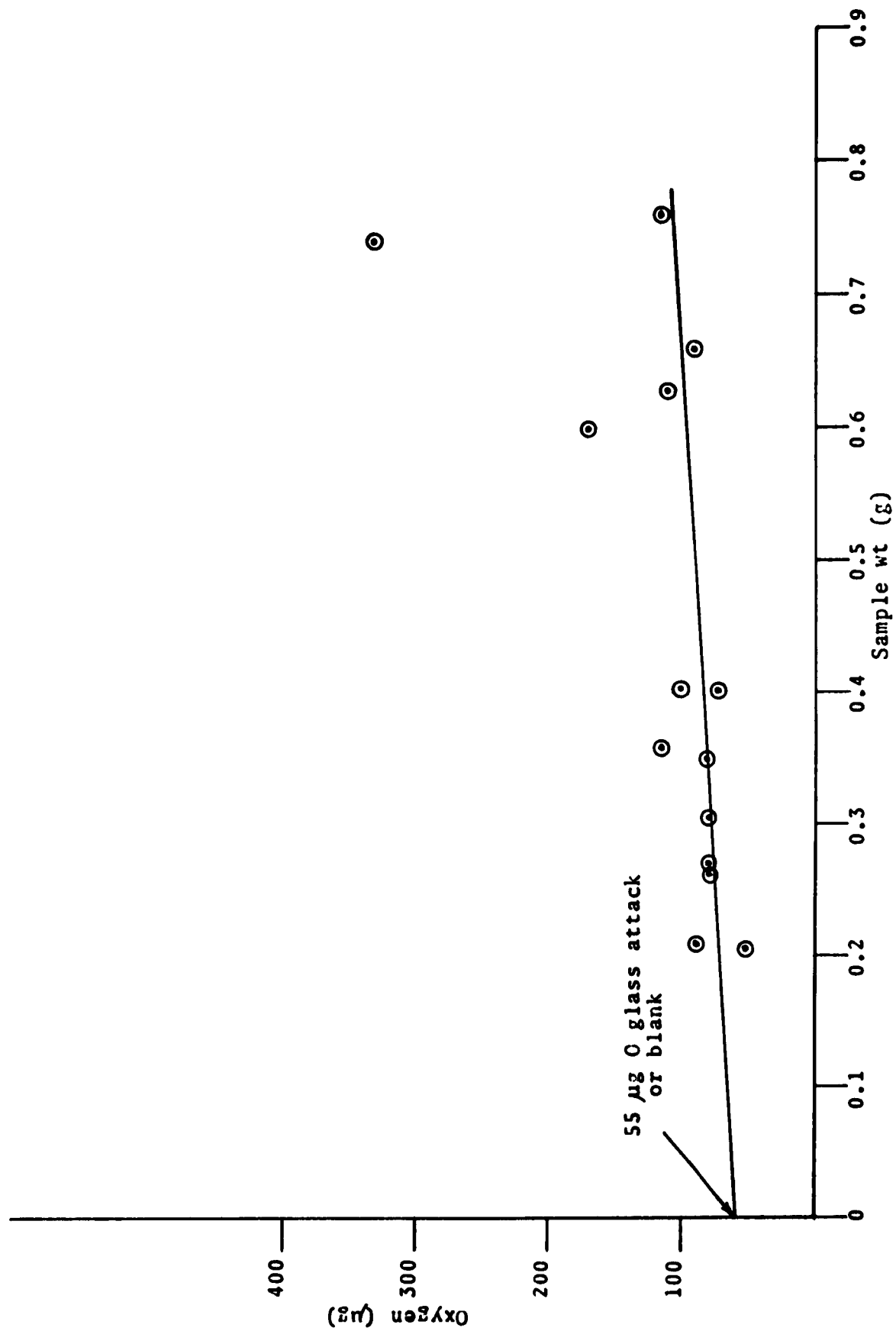
FIG 6 - OXYGEN BLANK RESULTING FROM GLASS ATTACK

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Stainless Steel Chamber

Ball and Socket Joint

Micrometallic Filter

Sight Glass

1/4" Stainless Steel Packed Valve

1

Glass Stopcock

2

Glass Adapter

Stainless Steel Chamber

Sight Glass

Sight Glass

1/4" Stainless Steel Packed Valve

3/64" Capillary

Glass Stopcock

3

4
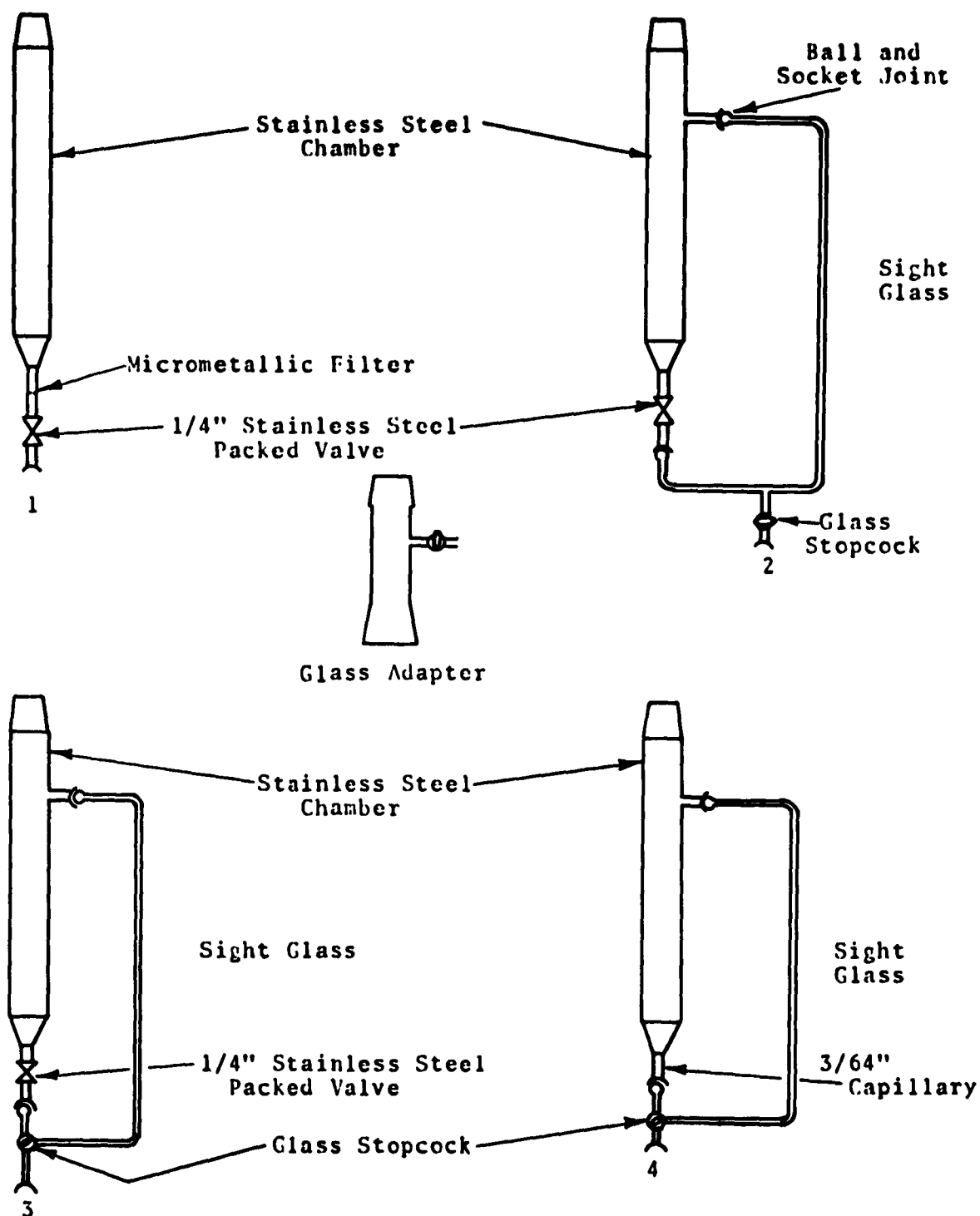
FIG 7 - METAL AMALGAMATION CHAMBERS

was used for all the metal chambers to permit visual examination of the sample during extraction. The samples were amalgamated by heating to 200°-300°C for 1-2 hours.

The main problem with the use of a metal amalgamation chamber was that the mercury level could not be observed when the amalgam was drained from the chamber. The various chambers were designed to eliminate this or control the level, and leave the oxide film in the chamber. Chamber #1 had a micrometallic filter in the drain leg, however, this plugged and could not be washed free of amalgam. A glass side arm was used as a level indicator on Chamber #2. This proved impractical since it was not possible to extract all the amalgam from the sight glass and to test for complete extraction of the amalgam from the chamber.

Chamber #3 had a three-way stopcock between the chamber drain valve and the sight glass. After the sample was amalgamated, the drain valve was opened and the amalgam level was indicated by the sight glass. The amalgam was drained from the chamber by the three-way stopcock. Subsequent extractions were made with 50 cc of mercury and the level was maintained by measuring the mercury. This arrangement permitted draining the amalgam and testing for complete removal of caustic without contamination from the sight glass after the level was established. As many as 10 to 14 mercury extractions (50 cc each) were required for a lithium free extract. Results were high (370-1000 ppm oxygen) even when the mercury extraction tested caustic free. It was decided that part of the problem was due to amalgam retention in the metal valve.

The drain valve was replaced with a 1-1/2 in. long by 3/64 in. ID stainless steel tube. The amalgam was drained from this chamber (#4) by the three-way stopcock in the same fashion as Chamber #3. A possible source of amalgam retention was removed by eliminating the valve but results were still unsatisfactory. Complete extraction of residual amalgam from the oxide samples was difficult, requiring two to three times the normal five extractions used in the standard amalgamation method. The results were two to three times higher than with the slow heating method in the glass apparatus. It is possible that the amalgam was being retained in micro-cracks and fissures in the metal walls. If such were the case, it would be difficult to remove traces of lithium with mercury flushing, but lithium could be extracted easily during the water rinse.

Because of time limitations, further work on developing a method for oxygen in lithium was discontinued. An

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indirect method for determining oxygen removal rates where gettering foils were exposed to lithium and analyzed for oxygen content was employed. This is discussed in greater detail under Purification of Lithium.

2. <u>Oxygen in Rubidium</u> - The feasibility of using the amalgamation method for analysis of oxygen in rubidium was subject to question at the beginning of this program. It had been shown in other work at MSAR that the amalgamation method was not applicable to the analysis of oxygen in cesium.[3] Standard additions of oxygen to cesium were not quantitatively recovered by the amalgamation method. Failure of the method is attributed to solubility of cesium oxide in cesium amalgam and/or mercury. A modified method using sodium amalgam as the extractant and based on the reaction:

$$Cs_xO_y + NaHg \longrightarrow Na_2O + CsHg$$
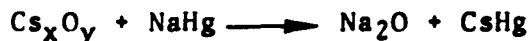
showed some promise but was fraught with operational difficulties and lacked good precision. The butyl bromide method also failed to give reliable and reproducible values of oxygen in cesium. With these facts in mind, it was assumed that the analysis of oxygen in rubidium could present a problem.

Rubidium cold trap #6 was charged with $\sim$ 2400 grams of 99.9% rubidium. Table 2 shows an analysis of this material. The vessel was heated to 1000°F and samples were extracted and analyzed by the standard amalgamation method. With the system operating isothermally, oxygen values of 19 and 17 ppm were obtained. The cold leg cooled to 80°F and the samples showed 5 and 6 ppm. (It was felt that rubidium oxide could not be cold trapped so little significance was placed in the difference in oxygen levels.)

The cold leg was reheated and the equivalent of 118 ppm oxygen as gaseous oxygen was bubbled into the rubidium charge. Initial analyses of the charge showed 93 ppm oxygen; after 16 days at 1000°F this value had dropped to 34 ppm. Incomplete recovery of the oxygen added was evident. It was of interest, however, that a steadily declining oxygen value was noted; this was attributed to hot trapping by the vessel walls. It appears that the amalgamation method will show trends but quantitative measurement is lacking.

Another oxygen addition equivalent to 153 ppm was made and the amalgamation method gave a result of 50 ppm. The expected level would have been 187 ppm. A subsequent addition of 126 ppm should have resulted in an apparent level of 166 ppm; the amalgamation method showed 86 ppm.

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It became obvious that an alternative method for the analysis of oxygen in rubidium was needed. Previous work with cesium had shown that oxygen will depress the freezing point of cesium (0.03°C per 10 ppm oxygen). It seemed likely that the same condition might exist with rubudium. A small vessel was fabricated and fitted with a thermometer well, thermistor well and valves. Provisions were made for the addition of quanti- tative amounts of gaseous oxygen. The vessel was filled with hot trapped rubidium, immersed in a constant temperature bath and a series of freezing point runs were made. The thermistor fed into a Sargent recorder (2.5 mv full scale) and permitted the recording of cooling curves, showing thermal arrests upon change of phase. Absolute temperatures were read on the Beckman thermometer to ± 0.002°C. Hot trapped rubidium exhibited a freezing point of 38.98°C. Oxygen addition totaling 20, 50, 100, 150, 250, 400, 650 and 900 ppm were made and the freezing point was measured at each level. A curve of oxygen concentration versus freezing point is shown in Figure 8. A freezing point depression of 0.0017°C per 1 ppm oxygen was observed. The curve appears to be linear to at least 900 ppm.

To expedite verification of the method, the rubidium cold trap was removed from the furnace, immersed in a constant temperature bath and a freezing point determination made. Re- sults indicated 100 ppm oxygen versus 40 ppm oxygen by amal- gamation. While the cold trap was in the constant temperature bath, 126 ppm oxygen was added as gaseous oxygen to the rubidium charge. The charge was heated to ∼150°F and then cooled through the freezing point. This determination showed 220 ppm oxygen — calculated value was 226 ppm oxygen. Amalgamation indicated 73-95 ppm oxygen. These results were encouraging and it was decided that the freezing point method would be used for the determination of oxygen in rubidium.

It was felt that this method was suitable for use under ideal conditions, i.e., a closely controlled constant temperature bath and alkali metal with low impurity content. Adaptation of this method to an operating system posed some problems. The primary problem was transfer of a representative sample from an operating system, at temperatures to 1000°F, to a vessel where a constant temperature environment could be maintained. Flushing of the vessel with each new charge of rubidium and maintenance of purity were associated problems.

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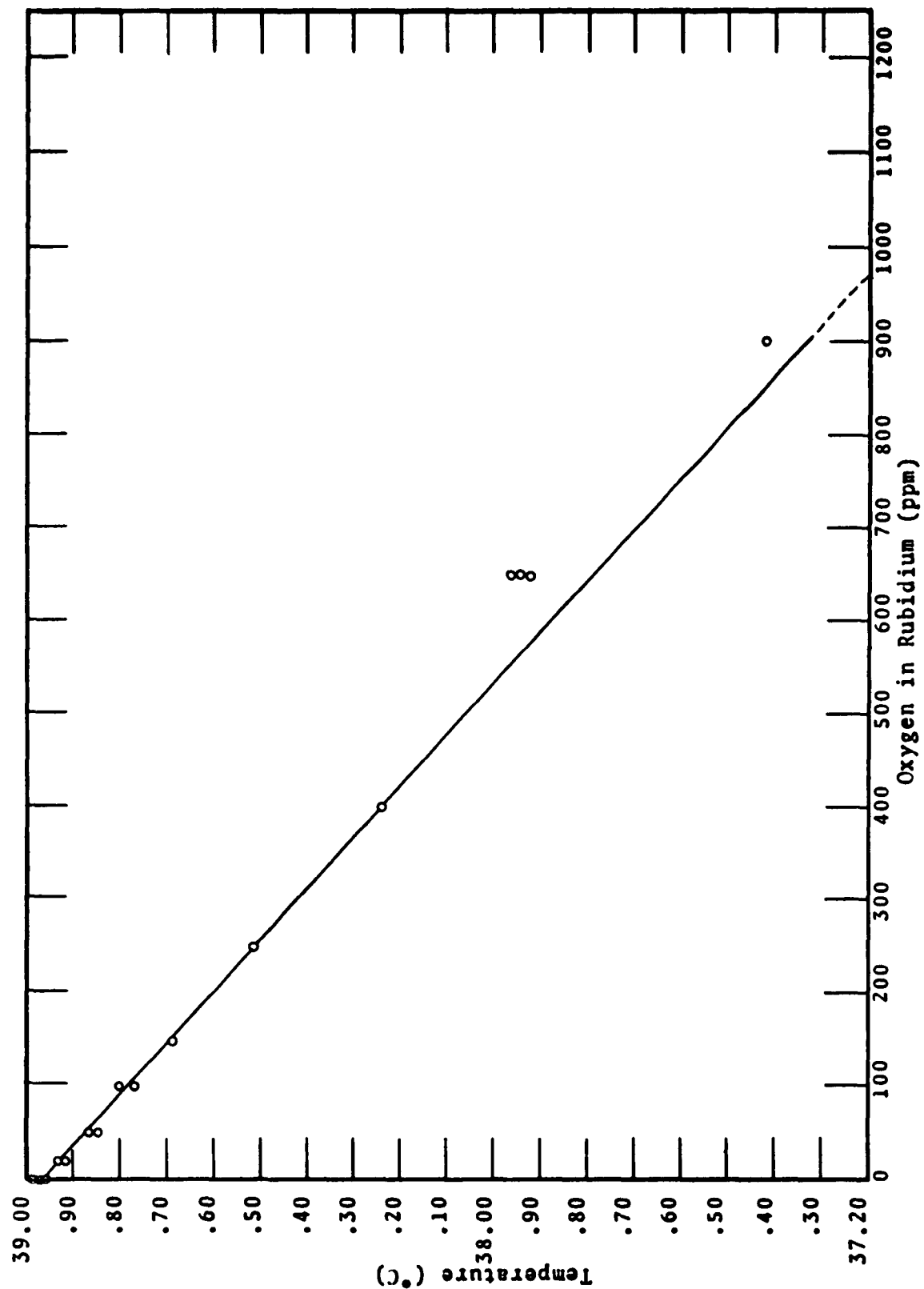
FIG 8 - FREEZING POINT DEPRESSION OF RUBIDIUM AS A FUNCTION OF OXYGEN CONCENTRATION

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The rubidium systems were modified with the addition of a stainless vessel with a capacity of $\sim$ 200 grams of rubidium (Figure 5). The freezing point vessel was connected to the rubidium system with 1/4-in. stainless steel tubing and contained within another vessel which served as a constant temperature bath. The freezing point vessel was isolated from the rubidium system with a 1/4-in. bellows seal valve. Provisions were made for maintaining an inert atmosphere over the freezing point charge and for transferring the charge by inert gas pressure. A complete description of the apparatus and operational procedures is given in Appendix A.

The performance of the system exceeded expectations and there is every reason to believe that the system could be adapted to any operating rubidium system as an in situ oxygen monitor; the same can be said for cesium, also. At present there are only two in situ oxygen monitors - the plugging indicator and Blake meter. The plugging indicator has performed well in sodium systems with the only objection being that any material which precipitates at lower temperatures can cause plugging. The plugging indicator cannot be used with rubidium or cesium because of the high solubility of the oxide at the melting point. The Blake meter is still in the development stage and has not gained much favor. The principal objection to the Blake meter is the stringent requirements of temperature control. With the freezing point device, a sample could be transferred from a selected location in the stream, a freezing point could be run and the charge could then be returned to the stream. It is likely that such a device could be programmed for automatic operation.

3. Analysis of Carbon and Nitrogen - Samples for carbon analysis are extracted from the system and transferred under inert cover gas to the analytical apparatus. The sample is reacted with water at 0°C and then acidified. Off gases during acidification are collected and measured mass spectrometrically for carbon dioxide and acetylene; carbonate and carbide levels are determined from these values. The sample is boiled to dryness and the dry salt is combusted in an atmosphere of pure gaseous oxygen. The carbon dioxide released is measured by mass spectrometry and the elemental carbon content is derived from this value. Typical sensitivities for carbonate, carbide and carbon are 10, 15 and 5 ppm respectively. A detailed description of the procedure is given in Appendix D.

Nitrogen samples are extracted from the system and transferred under inert gas to the analytical apparatus. The sample is reacted with water at 0°C and nitrides are converted to ammonia in the caustic solution. The solution is heated

and the ammonia which is driven off is collected in an acid solution. This solution is treated with Nessler reagent and concentration is determined by comparison with standards on a colorimeter. The method has a sensitivity of 2 ppm with a precision of ± 2 ppm. A detailed description is presented in Appendix E.

4. <u>Analysis of Hydrogen</u> - After a review of the literature on methods for hydrogen analysis in alkali metals, the isotopic dilution method described by Holt[4] for the analysis of hydrogen in sodium and NaK was selected for this study. The attractive feature of the isotopic dilution method is that complete recovery of hydrogen is not necessary since hydrogen concentration is determined by a hydrogen/deuterium equilibrium ratio.

A complete detailed description of the procedure is given in Appendix C. Some development work was required to adapt the method to the standard sampling technique used in this work. It was found that treatment of the nickel sample buckets was critical in obtaining a low reproducible blank. Pretreatment of nickel buckets used in dip sampling is a nitric acid etch followed by distilled water rinse and storage in a drying oven. Blank runs on the reaction tubes without nickel buckets represented 2 ug of hydrogen. Tube blanks with a sample bucket gave variable blanks up to 37 µg hydrogen. After several experiments which are listed in Table 5 it was determined that in order to obtain a reproducible blank the bucket must be degassed in vacuum at 450°C for at least one-half hour and not exposed to the atmosphere after this treatment. This resulted in reproducible blanks of 6-7 µg hydrogen. It was shown that exposure of a degassed bucket to the atmosphere for a few seconds resulted in a 2-fold increase of the hydrogen blank. The first sample tubes used were equipped with a 15 millimeter bore stopcock through which the sample bucket was lowered from the sampling apparatus under inert conditions. Since the sample apparatus also had a 15 millimeter bore stopcock perfect alignment of the stopcock was required in order to transfer a sample free of contamination from stopcock grease. Contamination showed in the mass spectrum as varying amounts of the mixed methanes of hydrogen and deuterium. The sample reaction tube was modified by replacing the 15 millimeter bore stopcock with a cap made from a 34/45 standard taper joint. The sample was then transferred to the reaction tube by the standard sampling method described in Appendix B.

Rubidium did not show any visible glass attack at the equilibrium temperature of 460°C, however, lithium etched the reaction tube where the metal contacted the glass. Lithium remaining on the outside of the bucket or spilling from the bucket

TABLE 5 - BLANK RUNS FOR HYDROGEN PROCEDURE

Blank Run No.	Bucket No.	Tube No.	H ug	Procedure
1	1	1	37	Standard cleaning, no special degassing.
2	1	1	6	Repeated after Run No. 1, not exposed to atmosphere.
3	1	1	6	Not exposed to atmosphere after Run No. 2, vacuum 450°C for 1/2 hour.
6	1	1	13	No treatment after Run No. 3, stored three (3) days in specimen bottle.
7	1	1	7	Repeated after Run No. 6, exposed to air then vacuum, 450°C for 1/2 hour.
4	4	1	14	Standard cleaning, vacuum, 450°C for 1 1/2 hours exposed to atmosphere when placed in tube.
8	5	2	7	Vacuum, 450°C for 1/2 hour not exposed to atmosphere.

during the equilibrium period resulted in the characteristic brown-black residue from alkali metal glass reaction. The residue hydrolyzed with water but left an etch mark on the tube. Lithium samples analyzed for hydrogen showed a hydrogen content of 15 ppm despite the obvious glass attack. A stainless steel thimble was fitted into a reaction tube as a possible solution to the glass attack but further work on hydrogen in lithium was deferred in favor of the work on oxygen removal rates by gettering.

B. Purification of Rubidium

1. <u>Introduction</u> - The freezing point method for oxygen in rubidium was selected as the analytical procedure for the purification study. Occasional analyses were made for carbon, nitrogen and hydrogen during the purification program. All oxygen additions were made as gaseous oxygen. A calibrated bomb was filled with oxygen and the gas was pressurized into the system with purified argon. The oxygen delivery tip was a hypodermic needle to provide small bubbles and assure complete reaction of the oxygen with rubidium. The needle was immersed to a level about 4 in. below the rubidium surface. Contents of the bomb were analyzed after the addition was completed to determine residual oxygen which had not been added to the rubidium charge.

2. <u>Cold Trapping</u> - Because of the high solubility of oxygen in rubidium at room temperature, it was assumed that cold trapping would not be feasible method of oxygen removal. However, there was no experimental evidence to validate this assumption, so the effect of cold trapping was evaluated. Table 6 shows the results of the experiment and Figure 9 presents an operational schedule of the rubidium cold trapping study.

The rubidium charge contained 10 ppm oxygen by freezing point determination. An oxygen addition of 174 ppm oxygen was made and an oxygen level lf 218 ppm was measured immediately after the addition. The vessel was maintained at 260°-290°F with the cold leg 20°-50°F higher. The leg was cooled to 70°F with the body at 300°F and no reduction in oxygen level was noted. The leg was reheated to 340°F and the oxygen remained constant. It was inferred from this that cold trapping was ineffective in removing oxygen from rubidium.

The vessel was heated to 800°F and the leg was maintained at 370°F. The procedure resulted in a reduction of oxygen from 205 to 105 ppm overnight and to 85 ppm in 24 hours. Five additional days under these conditions did not result in any additional reduction in oxygen level. It was assumed from these data that this reduction was a result of cold trapping by the stainless steel vessel walls - thermodynamically, iron and chromium should be capable of reducing rubidium oxide (Table 1).

TABLE 6 - RESULTS OF RUBIDIUM COLD TRAPPING STUDY

Date	Freezing Point (°C)	Oxygen (ppm) Freezing Point	Amalgamation	System Temperature[1] (°F)
8-20-63	39.14	10	10	620 (260)
	38.94	15	--	620 (260)
Added 174 ppm O_2 on 8-21-63				
8-21-63	38.56	218	29	260 (290)
8-22-63	--	---	120	260 (310)
	--	---	46	260 (310)
8-23-63	--	---	46	260 (310)
8-27-63	38.58	215	--	290 (310)
	38.59	205		
Cooled leg to 70°F with body at 300°F				
8-28-63	38.59	205		300 (70)
	38.51	250		300 (70)
	38.56	225		300 (70)
	38.52	250		300 (70)
Leg reheated to 340°F with body at 340°F				
8-29-63	38.59	205		
	38.59	205		
Body heated to 800°F				
8-30-63	38.78	105		800 (370)
	38.77	110		800 (370)
	38.81	90		800 (370)
	38.82	85		800 (370)
8-31-63	38.81	90		800 (370)
	38.82	85		800 (370)
9-3-63	38.84	70		800 (370)
	38.82	85		800 (370)
Added 154 ppm O_2				
9-3-63	38.43	295		300 (300)
	38.44	290		
Cooled leg to 70°F with body at 300°F overnight				
9-4-63	38.44	290		300 (70)
	38.44	290		300 (70)
Heated body to 910°F and run O_2 after 3 hrs at temperature				
	38.78	105		910 (310)
	38.77	110		910 (310)
9-5-63	38.73	130		880 (350)
	38.75	120		
	38.76	115		

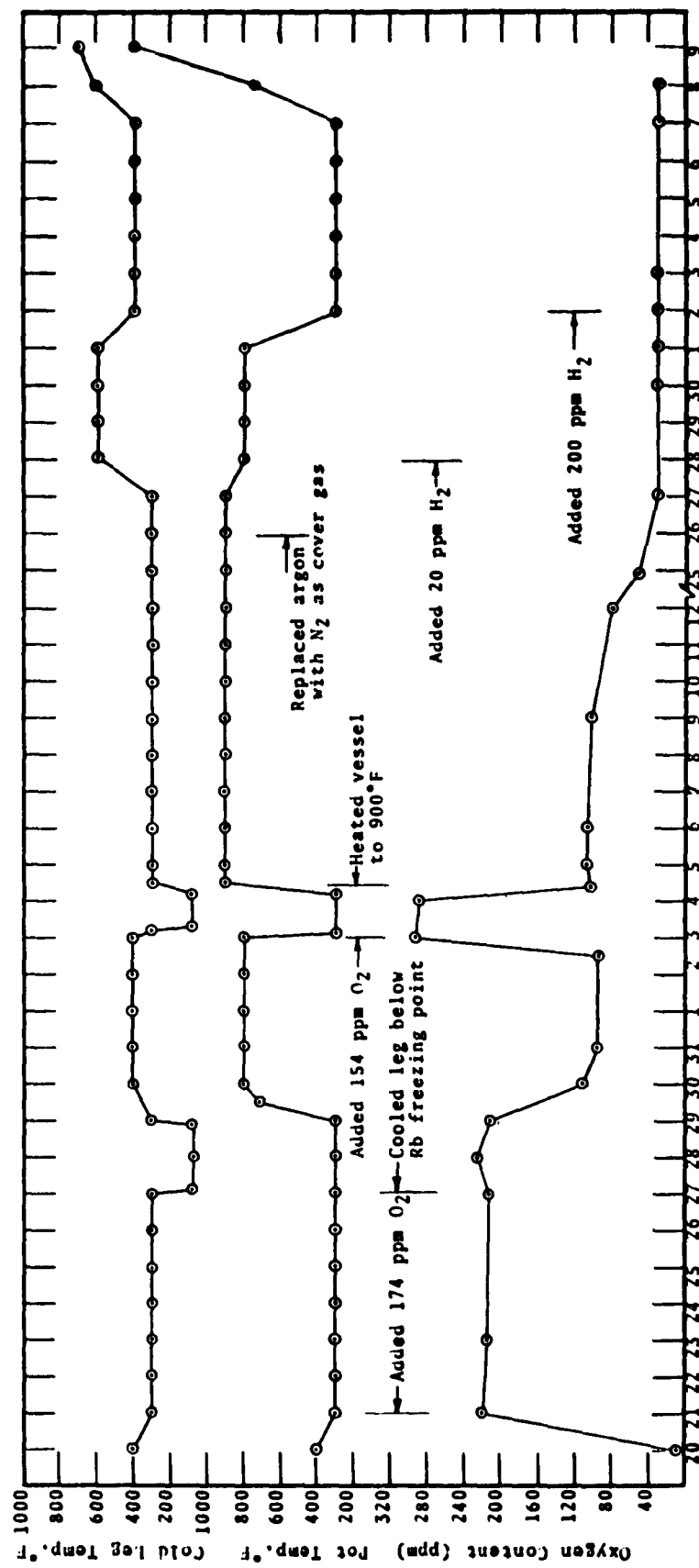(1) Numbers in parenthesis indicates cold leg temperature.

FIG 9 - OPERATIONAL DATA FOR RUBIDIUM COLD TRAPPING STUDY

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The system was cooled to 300°F and the equivalent of 154 ppm oxygen was added. Freezing point determinations with both the vessel and leg at 300°F indicated an oxygen content of 290-295 ppm. The leg was cooled to 20°F while the vessel remained at 300°F. No reduction in oxygen level was observed further verifying that cold trapping was ineffective.

The vessel was heated to 900°F and within 3 hours the oxygen level was reduced from 290 to ~110 ppm. After 20 days the oxygen level was reduced from 110 to 45 ppm. It was again assumed that this reduction was due to hot trapping by the vessel walls. An operational history is shown in Figure 9.

In summary, it was found that cold trapping was ineffective in removing oxygen from rubidium. This verifies the assumption that the high solubility of oxygen at the rubidium melting point would negate cold trapping as a method of purification. Reduction of oxygen level at elevated temperatures suggested that the stainless steel vessel was acting as a hot gettering medium.

3. Nitrogen in Rubidium - Before any attempts were made to study methods of removal of nitrogen from rubidium it was decided that the potential formation of rubidium nitride should be determined. It was also of interest to determine if the presence of nitrogen interfered in any way with the freezing point determination of oxygen in rubidium. Formation of rubidium nitride under normal conditions of operation was of some doubt. It has been shown that the nitride of sodium does not form when nitrogen is used as a cover gas on an operating system.

Argon cover gas used during the cold trapping study was replaced with nitrogen cover gas. An overpressure of 10 psig was maintained over the rubidium charge at 900°F. A freezing point determination indicated no change in freezing point and chemical analysis of the charge indicated zero nitrogen. Figure 9 presents an operational schedule. It was inferred from these results that a rubidium nitride does not form under normal operating conditions and that removal of nitrogen from rubidium will not be required.

4. Hydrogen in Rubidium - As with nitrogen, it was questionable whether rubidium hydride would form under normal operating conditions. Gaseous hydrogen equivalent to 20 ppm hydrogen was bubbled into the vessel at 900°F; hydrogen was injected through a hypodermic needle 4 in. below the surface. Unfortunately, neither a freezing point determination or a chemical analysis could be made for 3 days, so the result that

no hydrogen contamination was observed with either method was subject to question. During this 3-day period, any hydride which formed could have decomposed and hydrogen could have diffused through the vessel walls.

A second addition of hydrogen equivalent to 200 ppm hydrogen was made at 300°F. A freezing point run was made immediately and no change in freezing point was observed. Chemical analysis of the charge indicated no significant reaction with hydrogen. It was concluded from this that hydrogen is probably not a problem with rubidium. It would have been interesting to evaluate the behavior rubidium hydroxide but time did not permit. It is assumed that the hydroxide is reduced to the oxide and free hydrogen at elevated temperatures; this reaction occurs with sodium hydroxide in sodium and hydrogen is removed by pumping or flushing the system with inert gas.

5. Hot Trapping - Results from the cold trapping study indicated that rubidium oxide was reduced by the stainless steel vessel walls. Equilibrium concentration of oxygen in 900°F rubidium contained in stainless steel appeared to be approximately 35 ppm oxygen (Figure 9). At 1400°F, the equilibrium concentration was ~10 ppm oxygen. The rubidium hot trap was charged with 1360 grams of rubidium and 26.93 grams of zirconium foil 8.2 in. x 3.0 in. x 0.010 in. thick to compare the efficiency of zirconium runs with stainless steel. This amounts to a getter concentration of 2.05% by weight in rubidium. Results of this study are listed in Table 7 and plotted in Figure 10.

Freezing points were run on the as charged rubidium at 400°F and an oxygen content of 500 ppm was determined. After 3 days at 400°F the oxygen level was still 500 ppm.

The vessel was heated to 800°F and within 24 hours the oxygen level was reduced to 250 ppm. After 72 hours at 800°F, the oxygen was reduced to 190 ppm. A plot of these data (Figure 10) indicates that the oxygen level was still dropping so it is assumed that 190 ppm does not represent the equilibrium value under these conditions.

The temperature was increased to 1000°F and within 24 hours, the oxygen level had dropped to 80 ppm; after 72 hours the level was reduced to approximately 60 ppm.

The system was heated to 1400°F; the oxygen level was reduced to 10 ppm overnight. In an effort to determine the removal rate of oxygen at 1400°F, 179 ppm oxygen was added to the system (at 400°F) and the system was heated to 1400°F. Within 2 hours at 1400°F, the oxygen level was reduced from 300 to < 10 ppm oxygen.

TABLE 7 - RESULTS OF RUBIDIUM HOT TRAPPING STUDY

Date	Run No.	Freezing Point Temperature(°C)	Oxygen (ppm)	Temperature (°F)
9-11-63	2	38.56	214	800
9-11-63	3	38.59	206	
9-11-63	4	38.57	210	
9-12-63	1	38.63	188	800
9-12-63	2	38.62	190	
9-12-63	3	38.64	180	
9-13-63	1	38.83	78	1000
9-13-63	2	38.83	78	
9-16-63	1	38.85	66	1000
9-16-63	2	38.85	66	
9-16-63	3	38.86	58	
9-16-63	3	38.86	58	
9-17-63	1	38.965	2	1400
9-17-63	2	38.95	10	
9-17-63	3	38.972	0	
9-17-63	4	38.973	0	
9-18-63	1	38.96	2	1400
9-18-63	2	38.96	2	
Drained and refilled				
9-18-63	3	38.96	2	1000
9-18-63	4	38.96	2	
Added 179 ppm O_2				
9-18-63	5	38.05	300	400
9-18-63	6	38.48	268	
9-18-63	7	38.46	280	
Held at 400° overnight				
9-19-63	1	38.48	268	400
9-19-63	2	38.48	268	
9-19-63	3	38.94	10	1400
9-19-63	4	38.93	20	
9-20-63	1	38.93	20	
9-20-63	2	38.93	20	
9-20-63	3	38.92	24	
9-20-63	4	38.94	10	

(1) Hot trap contains 26.93 grams zirconium foil.

FIG 10 - RUBIDIUM HOT TRAPPING STUDY

Note: Hot trap contains 26.93 g Zr
foil 8.2 in. x 3.0 in. x 0.010
in. thick

Added 179 ppm O$_2$

System at 1400°F for 2 hrs

Temperature (°F)

Oxygen Content (ppm O$_2$)

September
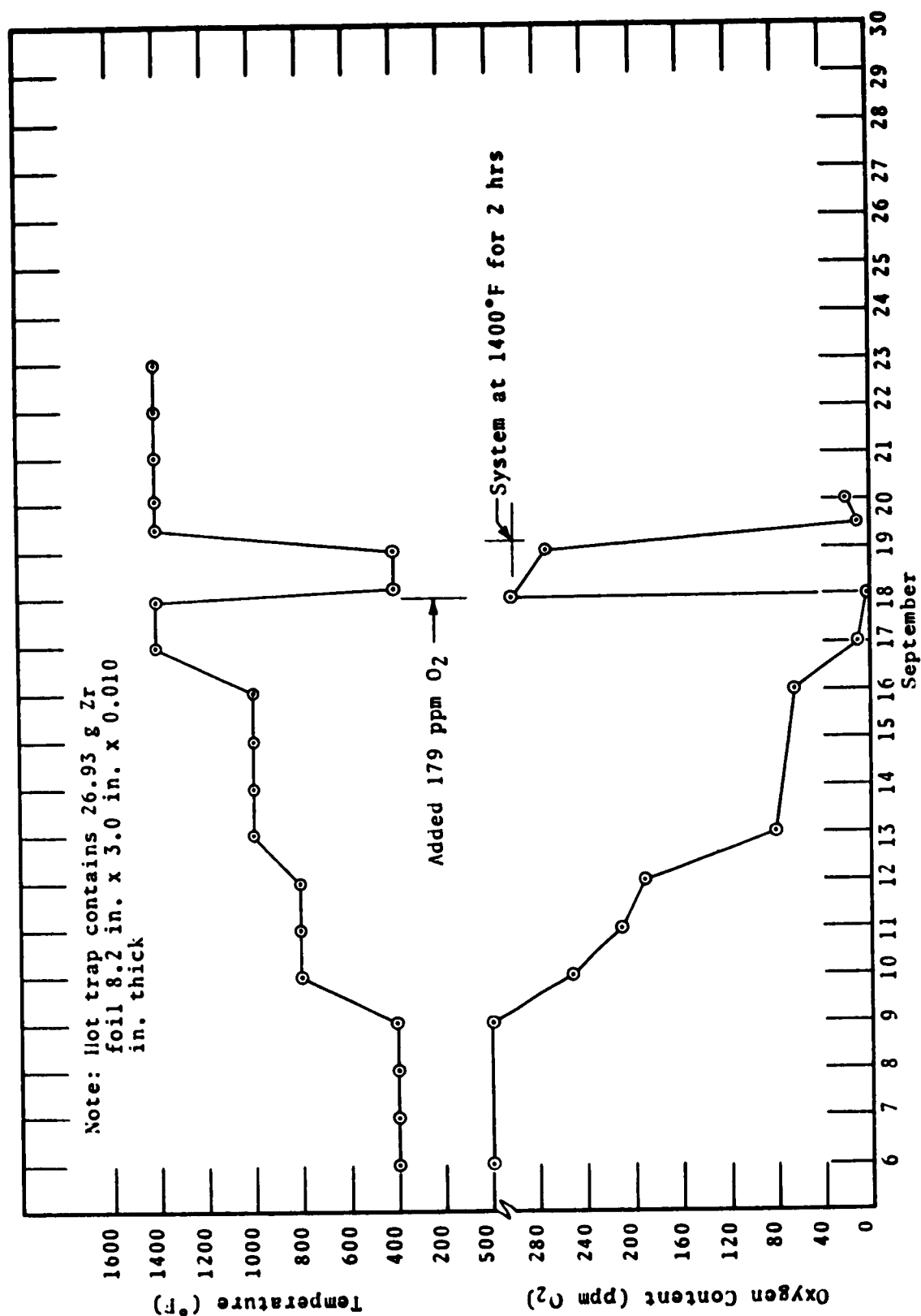
38

To determine the useful life of zirconium as a hot getter for rubidium, eight more oxygen additions equivalent to 170, 181, 166, 181, 168, 181, 141 and 110 ppm were made. This amounted to a total oxygen content, including the 500 ppm oxygen in the as charged rubidium, of 1977 ppm or 2.6 grams of oxygen.

After each addition, freezing point runs were made to determine the oxygen removal rate. The oxygen was reduced from 130 to 10 ppm in $<$2 hours at 1400°F after the last addition indicating that the zirconium was still functioning efficiently as a hot getter. Based on the reaction:

$$Zr + O_2 \longrightarrow ZrO_2$$

and a total of 26.9 grams of zirconium, complete reaction of the zirconium to zirconium oxide would remove 9.35 grams of oxygen. In this case, 2.6 grams of oxygen were removed or 28% of the zirconium was depleted. It has been a general rule of thumb in the design of hot traps for sodium purification to assume 25% as complete reaction of getter material with oxygen.

Results with zirconium indicated that the oxygen level in rubidium could be reduced to $<$10 ppm at 1400°F within 2 hours. It would be desirable in many cases to operate at a temperature somewhat below 1400°F. The use of titanium-zirconium alloy in gas systems has shown that these alloys will reduce oxygen levels at a lower temperature than either titanium or zirconium. Figure 11 is a plot of oxygen sorption rate constants as a function of temperature for a number of these alloys. An alloy of 50% zirconium-50% titanium was purchased and inserted into the rubidium hot trap. Oxygen additions were made and equilibrium values for a number of temperatures were determined. It was found that an equilibrium value of 10 ppm was attained at 800°F with the alloy compared to 1200°F for pure zirconium. A comprehensive study of removal rates was not made with the alloy because of the time schedule, but the oxygen was reduced from 180 to 50 ppm in 2 hours at 800°F and to 10 ppm in $<$2 days. In systems where heating to 1200°-1400°F may be impractical, the use of the alloy is recommended.

C. Purification of Lithium

1. Introduction - There is essentially no information available on the purification of lithium particularly with respect to oxygen. A number of investigators have used hot trapping, cold trapping and filtration as purification techniques but quantitative values are lacking because of the inability to analyze for oxygen. During the analytical development phase of this program, attempts were made to modify the amalgamation method for the analysis of oxygen in lithium. These attempts proved fruitless.
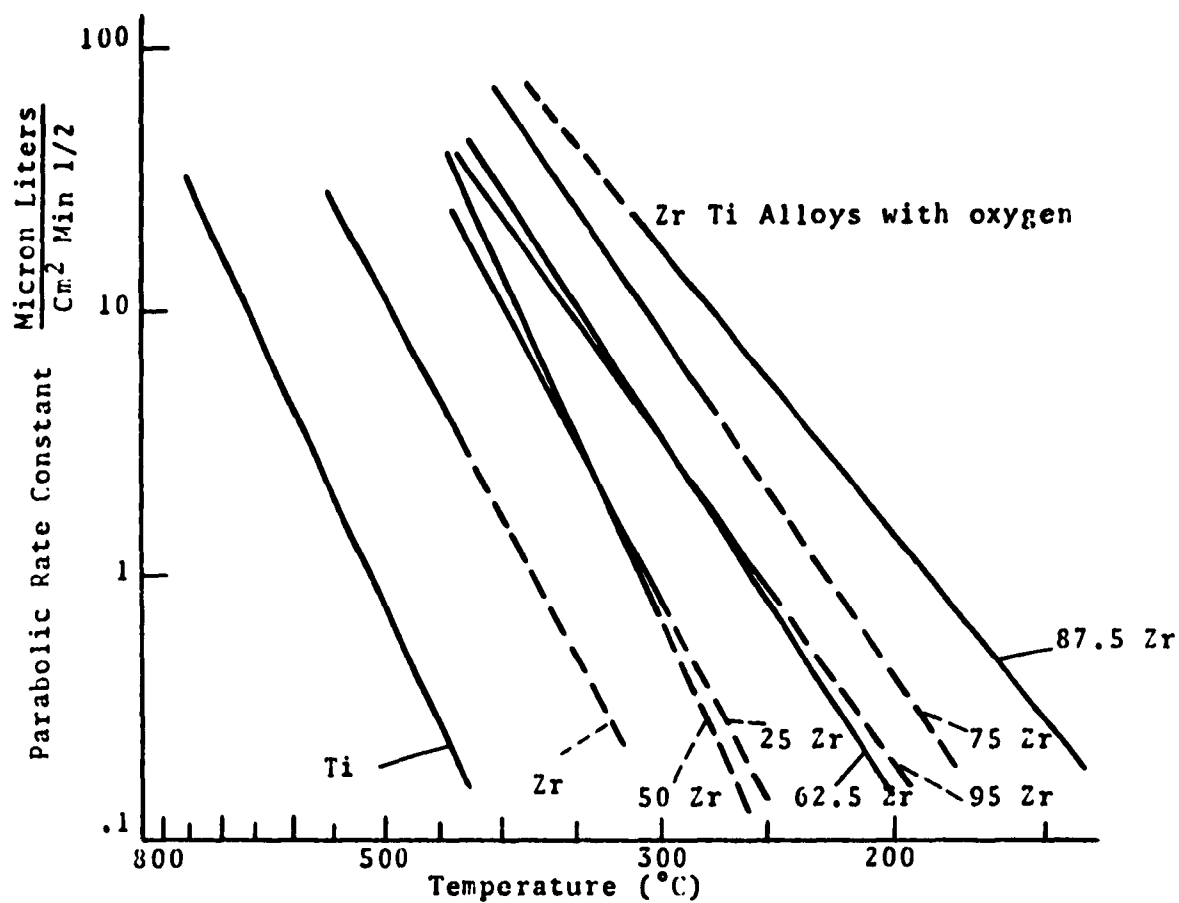
FIG 11 - VALUES OF THE RATE CONSTANTS FOR OXYGEN SORPTION
BY TITANIUM-ZIRCONIUM ALLOYS

In spite of the fact that oxygen analysis could not be performed, it was decided that the relative hot trapping potential of a number of getter materials should be established. As an alternate to analyzing oxygen in the lithium metal, analyses for oxygen as well as carbon, nitrogen and hydrogen were made of getter material tabs before and after exposure to lithium. In addition to this, metallurgical examination of the tabs was made to determine any changes in physical and/or chemical structure.

2. <u>Chemical Analysis of Tabs</u> - The materials which were chosen as potential getters were zirconium, titanium, yttrium, beryllium, thorium and uranium. These materials were obtained in 10-mil-thick sheets and were of the highest purity available. Tabs, 2 in. x 1/2 in. x 0.010 in., of each material were cleaned and stored under inert gas. Tabs of each material were then exposed to the same charge of lithium for 24 hours - the tab to lithium weight ratios were such that there was not a significant removal of oxygen from the lithium during the test. The lithium hot trap contained approximately 700 grams of lithium - if it is assumed that this was contaminated to the 100 ppm level, then the system contained 70 mg oxygen. Total oxygen removal by all of the tabs was approximately 14 mg oxygen or a calculated reduction in oxygen level from 100 to 80 ppm.

Table 8 shows the weight changes chemical analysis of the getter tabs before and after exposure to the lithium charge. Photomicrographs of the tabs are shown in Figures 12 to 17.

Zirconium tabs exposed at 1400°F showed a weight gain of 1.7 and 1.2 mg. Chemical analysis of the tabs showed increases in oxygen, carbon, nitrogen and hydrogen contents of the tab over the levels in the control. Weight gains based on these analyzed values were 1.88 and 1.66 mg. No evidence of surface films or corrosion was noted in the photomicrographs (Figure 12) of the zirconium tabs. However, significant grain growth was observed.

A titanium tab exposed at 1000°F experienced a weight loss of 0.18 mg but chemical analysis indicated a weight gain of 0.33 mg. One of the tabs exposed at 1400°F lost 0.31 mg (weight gain of 1.33 mg by chemical analysis) while the other tab showed a weight gain of 0.44 mg (1.65 mg by chemical analysis). The differences between weight change by weighing versus calculation from chemical analysis could be due to spalling either in the alkali metal or during washing after the test — this

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TABLE 8 - ANALYSIS OF GETTER MATERIAL EXPOSED TO LITHIUM

Material	Wt Before Exposure (g)	Wt After Exposure (g)	Wt Change (g)	Contaminant Levels								
				O_2 in Tab (ppm)	O_2 Removed (μg)	C in Tab (ppm)	C Removed (μg)	N_2 in Tab (ppm)	N_2 Removed (μg)	H_2 in Tab (ppm)	H_2 Removed (μg)	Total Wt Gain (mg)
Zr (control)	---	---	---	833	---	44	---	16	---	3	---	---
Zr (#1)	1.08155	1.08325	+0.00170	1700	936	222	192	670	705	45	45	1.878
Zr (#2)	1.05079	1.05200	+0.00121	1720	882	238	204	525	534	42	41	1.661
Ti (control)	---	---	---	1600	---	173	---	268	---	35	---	---
Ti (1,1000°F)	0.73828	0.73810	-0.00018	2035	321	183	7	62	---(2)	18	---(2)	0.328
Ti (2,1400°F)	0.72725	0.72694	-0.00031	3010	1030	304	95	550	205	33	---(2)	1.330
Ti (3,1400°F)	0.81999	0.82043	+0.00044	3230	1340	271	80	550	232	36	1	1.653
Y (control)	---	---	---	5100	---	446	---	510	---	62	---	---
Y (#1)	0.79350	0.78732	-0.00618	6380	230	383	---(2)	378	---(2)	>200	>110	>340
Y (#2)	0.83590	0.83680	+0.00090	5200	84	460	12	800	243	930	725	1.061
Be (control)	---	---	---	2195	---	64	---	142	---	22	---	---
Be (#1)	---(3)	---(3)	---(3)	3420	1250	262	205	810	680	21	10	2.145
Be (#2)	---(3)	---(3)	---(3)	2850	645	171	105	712	560	49	26	1.336
Th (control)	---	---	---	1320	---	115	---	126	---	124	---	---
Th (#1)	1.28358	1.20640	+0.02282	2360	1335	143	34	210	108	140	20	1.497
Th (#2)	1.33444	1.35930	+0.02486	5300	5300	469	470	1200	1430	15	---(2)	7.200
U (control)	---	---	---	442	---	340	---	63	---	2	---	---
U (#1)	3.38258	3.39484	+0.01226	570	433	330	---(2)	169	360	14	41	0.834
U (#2)	3.23161	3.24832	+0.01671	30[1]	---[1]	330	---(2)	130	217	15	36	0.253

[1] Sample too small for reliable analysis.
[2] No removal of contaminant.
[3] Severe spalling of surface coating.

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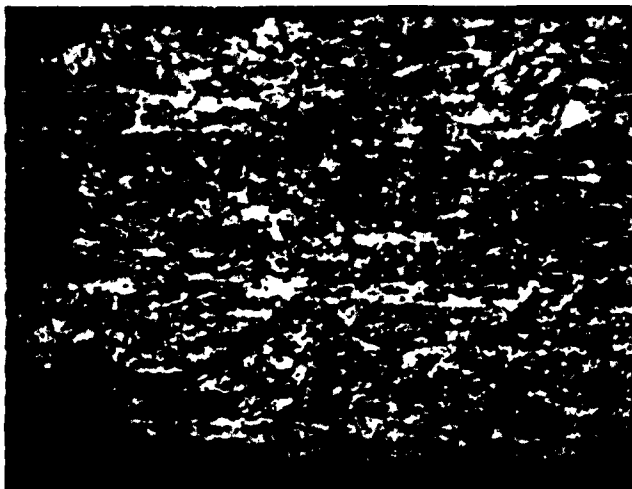
Zr cleaned

O_2	833
C	44
N_2	16
H_2	3

Zr #1   1400°F   24 hrs

O_2	1700
C	222
N_2	670
H_2	45

Zr #2   1400°F   24 hrs

O_2	1720
C	238
N_2	525
H_2	42

FIG 12 - PHOTOMICROGRAPHS OF ZIRCONIUM FOIL

43

Ti cleaned

O$_2$	1600
C	173
N$_2$	268
H$_2$	35
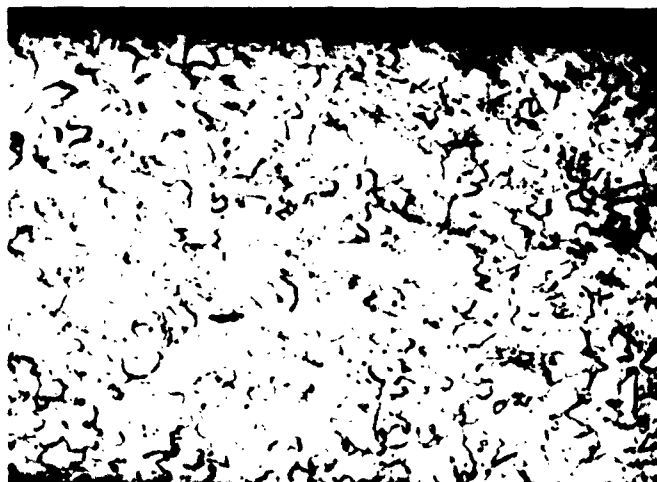
Ti #1   1000°F   24 hrs

O$_2$	2035
C	183
N$_2$	62
H$_2$	18
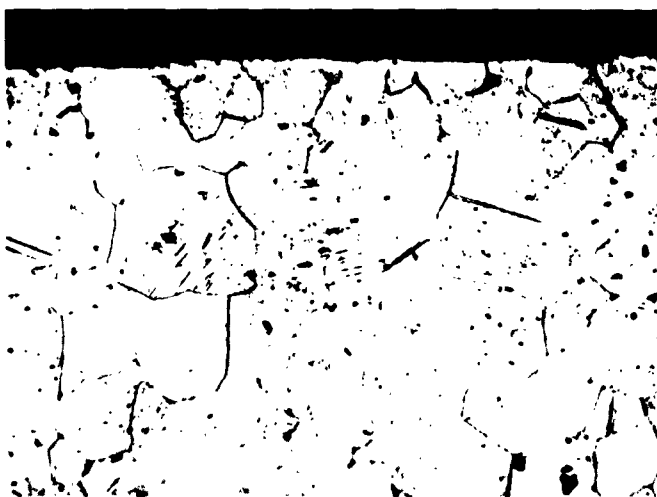
Ti #2   1400°F   24 hrs

O$_2$	3010
C	304
N$_2$	550
H$_2$	33
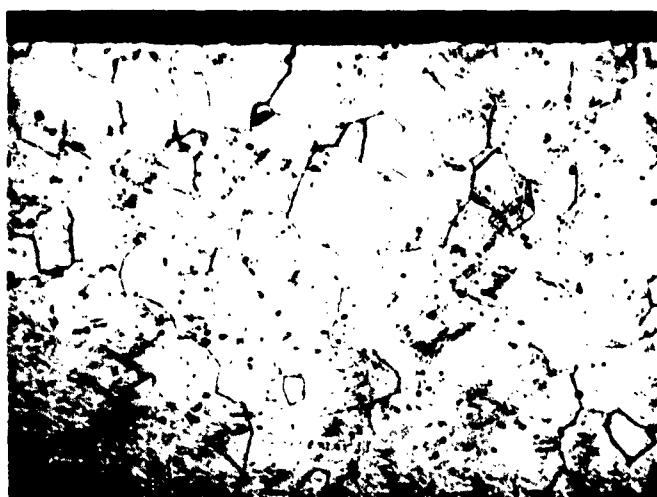
Ti #3   1400°F   24 hrs

O$_2$	3230
C	271
N$_2$	550
H$_2$	36

FIG 13 - PHOTOMICROGRAPHS OF TITANIUM FOIL

44

Y cleaned

O_2	5100
C	446
N_2	510
H_2	62

Y #1   1400°F   24 hrs

O_2	6380
C	383
N_2	378
H_2	> 200

Y #2   1400°F   24 hrs

O_2	5200
C	460
N_2	800
H_2	930

FIG 14 - PHOTOMICROGRAPHS OF YTTRIUM FOIL

Be cleaned

O_2 2195
C   64
N_2 142
H_2 22

Be #1   1400°F   24 hrs

O_2 3420
C   262
N_2 810
H_2 32

Be #2   1400°F   24 hrs

O_2 2850
C   171
N_2 712
H_2 49

FIG 15 - PHOTOMICROGRAPHS OF BERYLLIUM FOIL

Th cleaned

O_2	1320
C^2	115
N_2	126
H_2	124

Th #1 1400°F 24 hrs

O_2	2360
C^2	143
N_2	210
H_2	140

Th #2 1400°F 24 hrs

O_2	5300
C^2	469
N_2	1200
H_2	15

FIG 16 - PHOTOMICROGRAPHS OF THORIUM FOIL
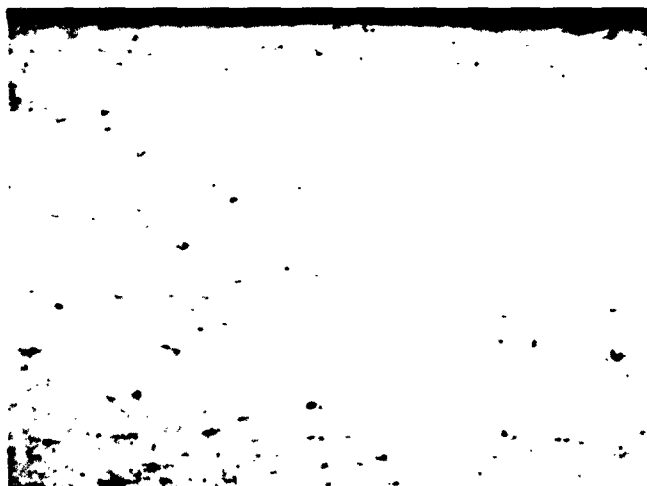
U cleaned

O_2	442
C	340
N_2	63
H_2	2
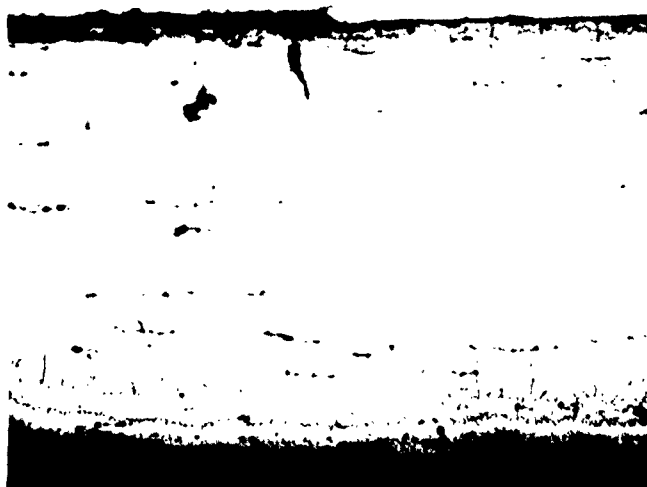
U #1   1400°F   24 hrs

O_2	570
C	330
N_2	169
H_2	14
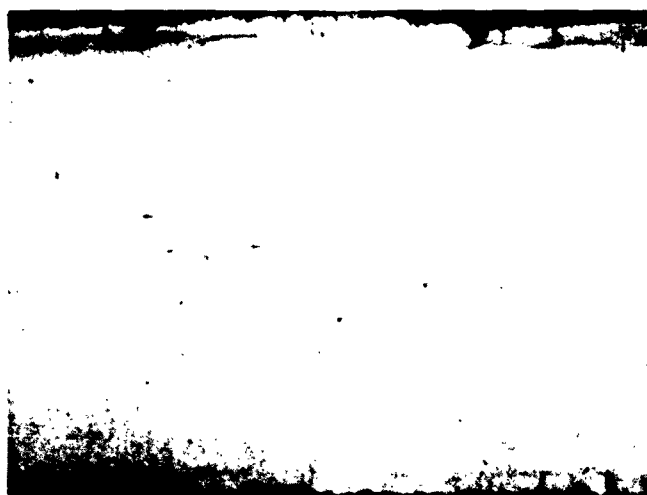
U #2   1400°F   24 hrs

O_2	30
C	330
N_2	130
H_2	13

FIG 17 - PHOTOMICROGRAPHS OF URANIUM FOIL

was particularly noticeable with beryllium. Photomicrographs
(Figure 13) of the titanium tabs showed no evidence of surface
film or corrosion. An increase in grain size was observed.

Yttrium tabs exposed at 1400°F showed weight changes
of -6.18 and +0.9 mg. Chemical analyses of these two tabs
indicated weight changes of 0.34 and 1.06 mg. The photomicrographs
(Figure 14) indicated a change in crystal structure. During
washing, a white gelatinous material was formed. This could have
resulted from hydrolysis of any coating and formation of yttrium
hydroxide.

No weight change measurements could be made on beryl-
lium because the loosely adhering film on the surface spalled
during washing. It was not possible to determine if this film
was firmly adherent during submersion in the lithium melt. Chemical
analyses indicated weight gains of 2.14 and 1.35 mg. Photo-
micrographs were taken of selected areas where the film remained
on the base metal surface. Figure 15 shows these films.

Thorium tabs showed weight gains of 22.8 and 24.9 mg.
However, chemical analyses showed lower gains of 1.50 and 7.20 mg.
The reason for divergence of weight values by the two methods is
not immediately evident; this could result from a combination of
contaminant reaction and at the same corrosion of the base metal
and/or the contaminant coating. Photomicrographs (Figure 16)
of these tabs showed significant surface coatings.

Uranium tabs showed weight gains of 12.3 and 16.7 mg.
Chemical analyses indicated weight changes of 0.83 and 0.25 mg.
Again the divergence between these results could be due to a com-
bination of reaction and corrosion. Some evidence of surface
coatings and corrosion can be seen in Figure 17.

In most cases, oxygen was responsible for the major
fraction of the weight gain. Nitrogen was the other major con-
tributor to weight gain. On the basis of chemical analyses, the
efficiency of the getter for specific contaminants would be
ranked as follows:

O_2	C	N_2	H_2
Th	Th	Th	Y
Ti	Zr	Zr	Zr
Be	Be	Be	U
Zr	Ti	U	Th
U	Y	Ti	Ti
Y	U	Y	Be

Although hydrogen is included in this list, it is felt that much of the increase in hydrogen content is due to hydride formation during cleaning of the tabs. Hydrogen is found as a reaction product of lithium and water.

On the basis of these chemical analysis done, thorium would seem to offer the most promise as a universal getter with zirconium ranking second. However, factors other than removal rates must be considered, the most important of these being spalling of surface coatings while the getter is immersed in lithium and alloy formations. These surface coatings, if re-leased to the main stream of an operating system, could result in plugging of narrow passages. Precipitation of one phase of the alloy in colder sections of the system could result in plugging, also.

With all these factors being considered, the logical choice of a universal getter for lithium would be zirconium. Zirconium exhibited the capability of removing all the contami-nants from lithium. Furthermore, the weight change data and chemical analyses agreed well suggesting that the contaminant coatings on the surface are strongly adherent (or that solid solution — of the contaminant composed in the base metal is sufficiently rapid so as to prevent spalling). Photomicrographs of the exposed tabs showed no evidence of corrosion.

Zirconium is available in high purity and in foil for fabrication of a high surface area hot trapping system. Zir-conium contained the lowest initial level of carbon, nitrogen and hydrogen and carbon second only to uranium in initial oxygen content. Impurities such as hafnium which could affect reactor operation and maintained at acceptably low levels in reactor grade zirconium. There are no problems with respect to hazards in handling zirconium foil. It can be fabricated into various shapes at room temperature in air. Zirconium should be cleaned before insertion into a system - in this study the following cleaning method was employed:

Solution - 95 parts: 95 parts water, 10 parts
           HF (40%).

Procedure- Immerse in pickling solution for
           30 seconds, remove and immediately
           rinse with water. Rinse with acetone
           and dry with an argon flush. Wrap
           in plastic film and store in a
           desiccator. Transport in covered
           vessels filled with argon.

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3. **Removal of Nitrogen from Lithium** - In addition to the tab exposure study on removal of nitrogen from lithium, a study was made on the effect of cold trapping in nitrogen removal. Results indicated that the lithium nitrogen level was reduced from ~ 3000 to ~ 900 ppm in 17 days with the cold leg operating at 300°F. This corresponds to the reduction of the nitrogen content from 1180 to 360 ppm or removal of 574 mg of nitrogen.

Results with zirconium tabs indicated the removal of ~ 0.6 mg nitrogen/gram of zirconium in 1 day. If the standard hot trapping ratio of 4% is applied, then 28 grams of zirconium would be used in the hot trap. This would result in the removal of 16.8 mg uranium/day or 286 grams in 17 days. On this basis it would appear that cold trapping would be a more rapid method of nitrogen removal, at least at the higher levels. This does not mean that cold trapping can reduce nitrogen to as low a level as hot trapping. Additional study would be required to clarify this point. It is inferred from these results that oxygen might also be removed by cold trapping, but lack of a suitable method of oxygen analysis in lithium prevented verification of this hypothesis.

IV. CONCLUSIONS

A. Rubidium

The freezing point depression method has been shown to be particularly sensitive to oxygen levels in rubidium. A minimum limit of detection of 10 ppm with a precision of $\pm$ 10 ppm is attainable with this technique. The most accurate and reproducible readings were taken with a Beckman thermometer, but a thermistor with readout on a Sargent recorder provided valuable information during the course of a cooling curve. It is felt that a more refined thermistor or a resistance thermometer could be used and perhaps provide a continuously recording oxygen monitor.

The device which was finally designed performed extremely well and required a minimum of operation. A typical run required 20-30 minutes for a complete analysis including heating of the freezing point device, transfer of rubidium to the device, making a freezing point determination, and interpretation of the results.

Cold trapping will not remove oxygen from rubidium. This was as expected because of the high solubility of oxygen in rubidium at the freezing point - the high solubility was verified during development of the freezing point depression curve. By inference, filtration would not remove oxygen from rubidium.

Hot trapping was established as an effective means of removing oxygen from rubidium. The stainless steel vessel walls effectively reduced the oxygen concentration. Equilibrium oxygen concentration with stainless steel at 800°F was 40 ppm; a temperature of 1400°F was required to reduce the oxygen level to < 10 ppm.

In practice, it would be undesirable to use the structural material of a system as a hot trap. This would lead to a reduction in system life and possibly to plugging because the oxide formed on the system walls could spall off. Zirconium reduced the oxygen content to < 10 ppm at 1200°F. The removal rate with zirconium was more rapid than with the vessel walls — oxygen was reduced from 270 to < 10 ppm in 2 hours.

It was found that 50%Zr-50%Ti alloy resulted in an equilibrium oxygen concentration of 10 ppm at 800°F. Oxygen was reduced from 180 to 50 ppm in 2 hours and to < 10 ppm in 2 days. Reduction of oxygen at lower temperatures is particularly desirable when heating to 1200°-1400°F is impractical. In an operating system, where temperatures of 1200°-1400°F are easily attainable, either zirconium or 50%Zr-50%Ti alloy could be used. However, in precharge purification system the alloy is recommended — the precharge system need be designed only for operation at 800°F.

It appears that removal of nitrogen and hydrogen from rubidium will not be required. A nitrogen pressure of 10 psi was maintained over a rubidium charge. No change in nitrogen content by chemical analyses was detected and no change in freezing point was observed. The addition of the equivalent of 200 ppm hydrogen produced no detectable change in either freezing point or chemical analysis.

In summary, the following conclusions are made on rubidium purification:

1. An in situ monitor for oxygen in rubidium is feasible based on the freezing point method.

2. Hot trapping is the recommended method for oxygen removal.

3. Either zirconium or 50%Zr-50%Ti can be used when the normal operating temperature of the system is 1200°-1400°F. When lower temperature operation is desirable, 50%Zr-50%Ti is recommended for oxygen removal.

B. Lithium

A suitable method for the analysis of oxygen in lithium was not established, however, it appears that the amalgamation method could be adapted for this analysis. Contact of lithium and/or the amalgam with glass must be avoided if reliable oxygen values are to be attained.

All of the getters which were evaluated removed oxygen from lithium. Nitrogen was removed by all of the getters except titanium. On the basis of the limited amount of data which was generated, zirconium is the recommended getter when considering the quantity of contaminant removed, adherent characteristics of surface film and corrosion of the getter material.

There was some indication that cold trapping would remove nitrogen from lithium. The rate of removal was low but this rate could be increased by using a forced circulation rather than a natural convection cold trap which was used in this study. It is assumed that if nitrogen in lithium can be cold trapped that the same is true of oxygen. This assumption is based on the temperature dependent solubility of oxygen in lithium. Levels to which these contaminants can be reduced are not known.

LIST OF REFERENCES

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3. Tepper, F. and Greer, J., Factors Affecting the Compatibility of Liquid Cesium With Containment Materials, Part I, ASD-TDR-63-824, MSA Research Corporation, Callery, Pa. (September 1963).

4. Holt, B.D., Determination of Hydrogen in Alkali Metals by Isotope Dilution Methods, Anal. Chem. 31, p 51 (1959).

APPENDIX A

FREEZING POINT METHOD

A. Rubidium Cold Traps

A schematic diagram of the freezing point apparatus is shown in Fig 5. The unit was constructed of Schedule 40 Type 316 stainless steel. The interconnecting piping was 1/4 in. stainless steel tubing and contained a 1/4 in. Hoke bellows seal valve. The small pot which contained the rubidium on which the freezing point was to be measured was 1-3/4 in. diam, by 3 in. high. Two dip wells into this pot contained the thermistor and a Beckman precision thermometer. These wells were made of 1/4 in. tubing and 1/2 in. tubing, respectively. An overflow reservoir was located just above the small pot containing the rubidium and provided a freeze seal if the liquid metal overfilled freeze point determination chamber. The mineral oil bath was a 6-1/2 in. diam. by 8 in. high vessel which contained a cooling coil and an electric immersion heater. A cover gas of argon was provided with a valving arrangement which permitted evacuation to atmosphere conditions as well as pressurization after the unit was charged.

An operational procedure for the unit is described as follows:

1. The cold trap and freezing point apparatus is maintained under 10 lb argon pressure.

2. With valves V-2 and V-3 closed, V-1 is opened to vent the freezing point apparatus by allowing the excess pressure to bleed through the mercury bubbler. This bubbler serves as a seal against atmospheric contamination.

3. The 1/4 in. interconnecting piping and oil bath is heated to about 110°-120°F.

4. Valve V-1 is closed and V-4, a bellows seal valve is opened and the liquid is forced into the freezing point apparatus by the ΔP between the two vessels.

5. Valve V-3 is opened equalizing the pressure between the two vessels allowing the rubidium to return to the cold trap.

6. This procedure is performed three times to assure a representative sample has been charged to the freezing point apparatus. Valve V-4 is closed, holding the charge in the freezing point apparatus.

7. The mineral oil bath surrounding the freezing point apparatus is then cooled to about 41°C by circulating water through the coils which are immersed in the mineral oil. The cooling water is then turned off and allowed to air cool slowly through the freezing point.

8. The freezing point is recorded using a thermistor feeding to a 2.5 mv recorder. The absolute freezing point is determined to 0.002°C with the Beckman precision thermometer.

9. After the freezing point has been determined, the charge is reheated by heating up the oil bath with an immersion heater, and by closing valve V-5, and venting the cold trap through V-6, rubidium is returned to the cold trap by opening valve V-4.

10. The procedure is repeated to provide duplicate results.

The time required for this procedure is normally less than 1 hour.

B. Rubidium Hot Trap

A unit similar to the one shown in Fig 5 was constructed and installed in rubidium hot trap No. 3. This unit was operated by the procedure described above.

C. Lithium Hot Trap

A third unit was constructed and installed in the rubidium hot trap No. 4. This freezing point unit was also similar to the one described in Fig 5. However, with the high freezing point of 180.7°C for lithium, the interconnecting piping required more heating. Electrical heaters were attached to the piping and valves and a stainless steel shield applied around the piping. A thermocouple was applied to strategic locations to insure adequately high temperatures along the pipe for the flow of lithium. The piping and heaters were insulated with asbestos.

The oil bath which was used to heat the freezing point apparatus contained a high boiling wax, replacing the mineral oil. The procedure for determining the freezing point was similar to the procedure described above except considerably more time was required to heat up the piping and bath and cooling rate was reduced at the higher freezing point for lithium, i.e. 181°C.

This unit operated satisfactorily except for the bellows seal which required additional heating and the stem required replacement following a freeze up.

APPENDIX B

ALKALI METAL SAMPLING AND OXIDE ANALYSIS AMALGAMATION METHOD

I. INTRODUCTION

A. Summary

A sample of alkali metal is reacted with mercury — the metal amalgamates ,and the insoluble oxide remains as a residue on the amalgam surface. The amalgam is drained off and the residual oxide is washed free of amalgam by subsequent additions of mercury. The oxide is then titrated with 0.01N hydrochloric acid. Sample size is determined by titrating the amalgam with 2.5N hydrochloric acid.

B. Reagents

> Mercury - triple distilled or equivalent
> Phenolphthalein - dissolve 0.2 g of phenolphthalein
>   in 50 ml of ethyl alcohol and add 50 ml of
>   water
> Hydrochloric acid - 2.5N
> Hydrochloric acid - 0.01N
> Sodium hydroxide - 2.5N
> Sodium hydroxide - 0.01N

C. Equipment

Oxygen Sampling and Analytical Apparatus - MSA Research Corporation Apparatus, Fig 18, consists of the following components: sampling apparatus, amalgamation chamber, amalgamation head, 1-1/2 in. NPS to 34/45 standard taper inner joint brass adapter, liquid level indicator, nickel sample bucket, nickel wire, 1/4 in. stainless steel dip rod and Tesla coil.

Argon Supply - Argon cover gas is purified by bubbling through a special purification train consisting of hot (600°F) NaK, cold NaK and zirconium chips at 1200°-1400°F. An MSAR Model 15H Gas Purification System is equipped with a pressure regulator and two copper lines with short lengths of flexible brass tubing. Cover gas connection to the glass apparatus is through a brass 12/5 standard ball joint at the 1/4 in. valve on the end of each flexible brass hose. The gas pressure is adjusted to 2-3 psi during sampling.

Vacuum Coupling
1/4" Tubing

S 34/45

11 cm

Brass
15 mm

O Ring
Seal

Glass
15 mm

Ni Wire
Screw
Clamp

Vacuum
Tubing

1/4" OD
SS
Tubing

50 cm

32 mm

30
cm

Stopcock
2 mm Bore

Stopcock
15 mm Bore

2 mm Capillary
Tubing

S 34/45

S 34/45

S 12/5

Course Fritted
Glass Disc

Ni Bucket

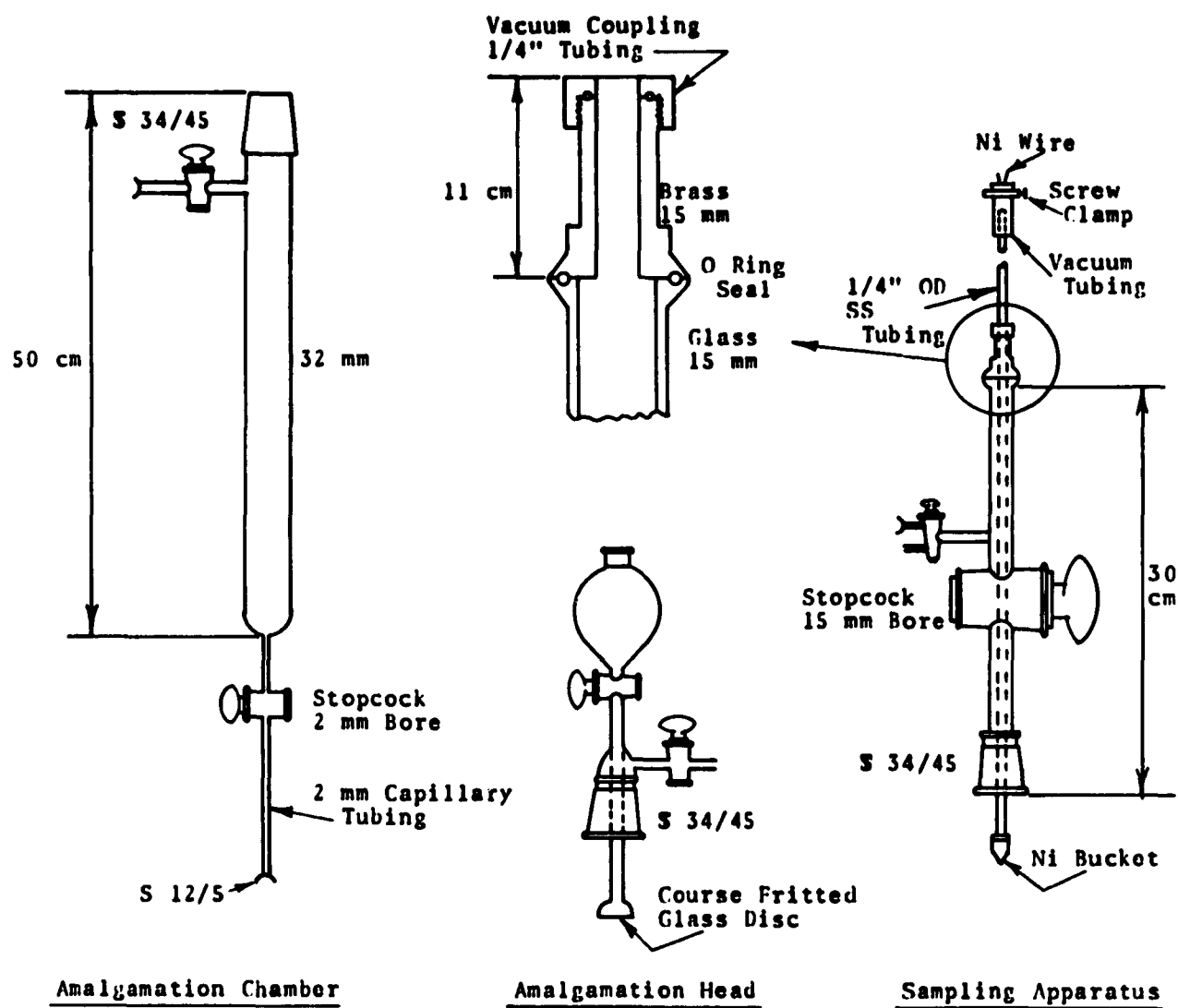Amalgamation Chamber

Amalgamation Head

Sampling Apparatus

FIG 18 - SAMPLING AND AMALGAMATION APPARATUS

II. PROCEDURE

A. Sampling

Secure the amalgamation chamber on the support stand and place the amalgamation head on the chamber. Assemble the sampling apparatus according to Fig 18. Grease all stopcocks lightly using particular care on the large 15 mm bore stopcock so that excess grease will not accumulate at the opening. Fold a sufficient length of nickel wire in two and slide a sample bucket to the closed end. Twist the open ends slightly and run the wire through the 1/4 in. stainless steel dip tube and out the 3 in. length of 1/4 in. rubber vacuum tubing. Pull the nickel bucket up tight against the dip rod and secure by closing the screw clamp on the rubber tubing. Hold the ends of the wire with pliers while tightening the screw clamp and wind the loose end around the thumb screw of the clamp.

Apply a small amount of stopcock grease to the brass adapter and place the sampling apparatus on the adapter. Attach one argon line to upper outlet of three-way stopcock. Attach the vacuum line to the lower outlet, open the three-way stopcock and evacuate the sampling apparatus. Flame the apparatus, dip rod and argon adapter back to valve to remove moisture. Allow to cool while evacuating for 5 minutes, turn three-way stopcock to argon and fill apparatus to the regulated pressure. Evacuate and fill with argon 3 times; allow 1 minute evacuation and 1 minute pressurizing each time. (Use caution when breaking vacuum; do not allow argon pressure to fall to zero.) After final pump out fill with argon and wait 3 minutes before dipping the sample.

Attach one lead of level indicator buzz box to the dip rod and other lead to the sample vessel. Reduce pressure in the sample vessel to that of the sampling apparatus and open the vessel sampling valve. Lower bucket 3 or 4 inches at a time and avoid touching the sides. When bucket touches liquid metal as indicated by the buzzer lower into metal the height of the bucket, being careful to prevent any liquid metal from entering the open end of the dip rod. Raise the bucket until clear of metal, wait a few seconds then lower until tip of bucket touches. This removes the drop of liquid metal which drains from the wetted sides of the bucket. Raise the bucket carefully until clear of the adapter, close the vessel sampling valve and allow the sample to cool. For lower melting metals (Rb-Cs), wrap a cloth containing solid carbon dioxide around the outside of the apparatus near the sample.

While waiting for sample to solidify, place the amalgamation chamber-amalgamation head assembly close to the sample vessel within reach of the argon lines. Attach the other argon line to the amalgamation chamber drain stopcock, and the vacuum line to the side arm stopcock. Evacuate and flame the assembly to the argon line valve and check for leaks with the Tesla coil. If there are no leaks, fill apparatus with argon.

Raise the sample above the 15 mm stopcock and close the stopcock. Remove the mercury reservoir from the amalgamation apparatus and transfer the sampling apparatus from the vessel to the amalgamation chamber, maneuvering the argon line to avoid any strain on the assembly. Evacuate and flame the amalgamation chamber up to the 15 mm stopcock of the sampling apparatus. Secure the sampling head to the amalgamation chamber with springs or rubber bands. Pressurize with argon and evacuate 3 times using the same procedure as was used on the sampling apparatus. After the last evacuation, pressurize with argon and leave the drain stopcock and argon line valve open to the chamber. Open the 15 mm bore stopcock and lower bucket until it rests on the bottom of the amalgamation chamber. Avoid touching any part of the apparatus with the bucket while it is lowered into the chamber. Open the screw clamp on the dip rod, untwist wire and release bucket by extracting the wire. Close screw clamp and pull rod clear of amalgamation chamber.

Remove sampling apparatus from the chamber and quickly place the amalgamation head in place with both stopcocks open and argon flowing up through the drain stopcock. Check argon flow out the amalgamation head outlets using the Tesla coil and adjust so that a steady flow is maintained. Secure amalgamation head to chamber with rubber bands or springs and purge through apparatus for 3 minutes. Close stopcocks of amalgamation head, allow pressure to build up the regulated pressure (2-3 psig) and close drain stopcock.

B. Amalgamation

Add 50 ml mercury to the mercury reservoir and attach a gas pressure line to the opening. A rubber stopper with a short piece of glass tubing can be used for this connection. Admit the mercury to the amalgamation chamber by applying 10 psi to the reservoir and opening the stopcock. Mercury is forced through the fritted disk in a fine spray. Do not push all the mercury into the chamber but allow several milliliters to remain in the mercury reservoir. (When amalgamating potassium apply heat by lightly flaming the chamber.)

When the sample is completely amalgamated,drain off the amalgam into a 600 ml beaker containing 25 ml of 2.5N HCl and 75 ml of water. Retain a small reservoir of mercury to prevent loss of the oxide residue. Repeat mercury addition and mixing five times. On the fifth extraction, drain the mercury into a 100 ml beaker containing 5 ml of water and a few drops of phenolphthalein to test for complete amalgam extraction. If the indicator shows caustic still present, continue extractions until an alkali free extract is obtained. More than 6 extractions is unusual and should be noted. Add an excess of 2.5N HCl (if not already in excess) to the amalgam in the 600 ml beaker and stir to react the amalgam.

C. Determination of the Oxide

Adjust ~150 ml of CO_2 free distilled water to pH 7.0 with 0.01N NaOH on a pH meter and place in a plastic wash bottle. Remove the amalgamation head from the sampling apparatus and wash the oxide out of the chamber with ~20 ml of pH 7.0 water. Pour the first wash into a 150 ml beaker being careful not to pour out the mercury or the bucket. Transfer the mercury and the bucket to a second 150 ml beaker. Some mercury will remain in the capillary - do not remove it. Rinse the bucket and mercury with water and decant the washings into the first beaker. Rinse out the chamber with 2 more 20 ml rinses and add this to the total rinses. Place the solution on the magnetic stirrer and immerse the electrodes of the pH meter. Place a nitrogen purge tube near the surface of the solution to prevent CO_2 absorption from the atmosphere. After recording the initial pH, add small increments of the 0.01N HCl and record, in tabular form, the increments (Δml), total volume added (ml), and pH, according to the following example.

Δml	ml	pH	ΔpH	ΔpH/Δml	
	0	9.75			
0.5	0.5	9.25	.50	1.0	
0.1	0.6	9.00	.25	2.5	
0.02	0.62	8.90	.10	5.0	
0.02	0.66	8.65	.15	7.5	
0.02	0.68	8.43	.22	11.0	
0.01	0.69	8.24	.19	19.0	
0.01	0.70	8.00	.24	24.0	
0.01	0.71	7.70	.30	30.0	end point
0.01	0.72	7.45	.25	25.0	
0.02	0.74	7.21	.24	12.0	

Between additions calculate the $\triangle pH$ and $\triangle pH/\triangle ml$ ratio. The end point to the nearest 0.01 ml is taken at the greatest $\triangle pH/\triangle ml$ value.

D. Determination of Sample Size

To the reacted amalgam, add 10 ml of 2.5N NaOH or sufficient amount for an excess as indicated by phenolphthalein. Back titrate the excess sodium hydroxide with 2.5N HCl.

E. Calculations

$$\frac{ml \times 0.01N \; HCl \times .008}{ml \times 2.5N \; HCL \times metal \; equiv.} \times 100 = wt \; \% \; O$$

$$(ml \times 2.5N \; HCl) - (ml \times 2.5N \; NaOH) \times metal \; equiv. = sample \; wt.$$

$$\frac{ml \times 0.01N \; HCl \times 0.008}{sample \; wt.} \times 100 = wt \; \% \; O$$

APPENDIX C

DETERMINATION OF HYDROGEN IN LIQUID METALS

I. INTRODUCTION

A. Summary

Deuterium is added to an alkali metal sample in a special reaction tube and equilibrated with sample hydrogen by heating at 460°C. The H/D ratio is calculated from the net outputs of mass 2, 3 and 4 peaks on a mass spectrometer. The hydrogen concentration of the sample is determined from this value.

B. Reagents

    Hydrogen
    Deuterium - The Matheson Company, Inc.
    Hydrogen deuteride - Prepared by the action of heavy
                water on lithium aluminum hydride
    Methanol
    Phenolphthalein indicator
    Hydrochloric acid - 2.5N

C. Equipment

Hydrogen Apparatus - The schematic of the system used to admit deuterium to the sample is shown in Fig 19. Deuterium is introduced to the apparatus from a cylinder fitted with a low pressure regulator and gauge.

Sample Tube - Several tubes are required. The tube serves as the reaction vessel and the mass spectrometer sample bulb. The 32 mm OD tube is made by sealing off the end of a 34/45 standard taper inner joint to give a total length of 20 cm. The cap is made from the outer joint. Fig 19, part G shows a schematic of the tube. The tube attaches to the apparatus and the mass spectrometer inlet system by means of the 12/30 standard inner joint on the cap sidearm.

Furnace - Tube type furnace capable of 500°C operation.

Vacuum Pump - A liquid nitrogen trap is placed in the line between the system and pump.
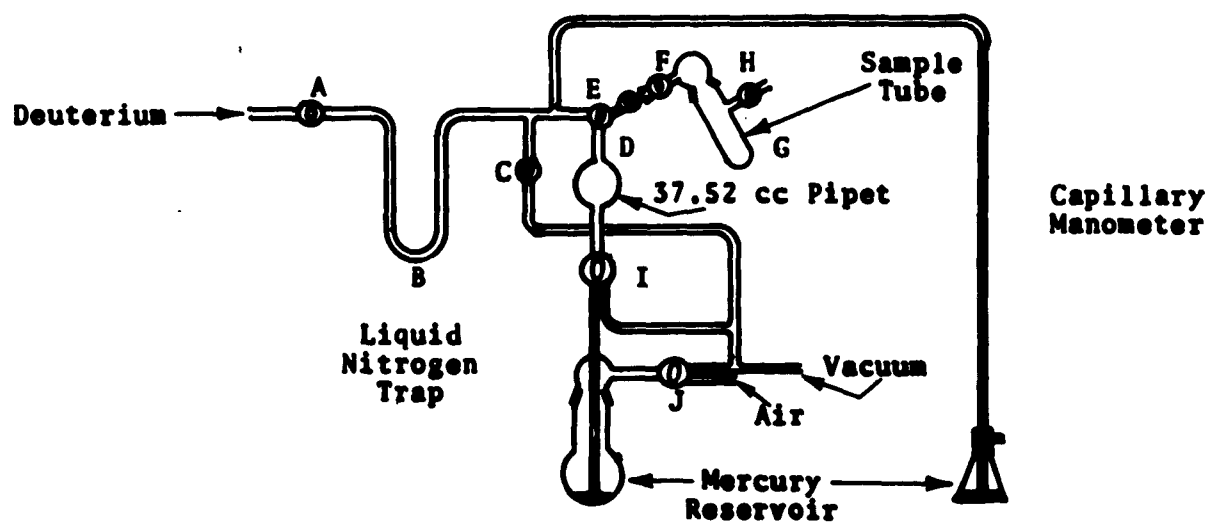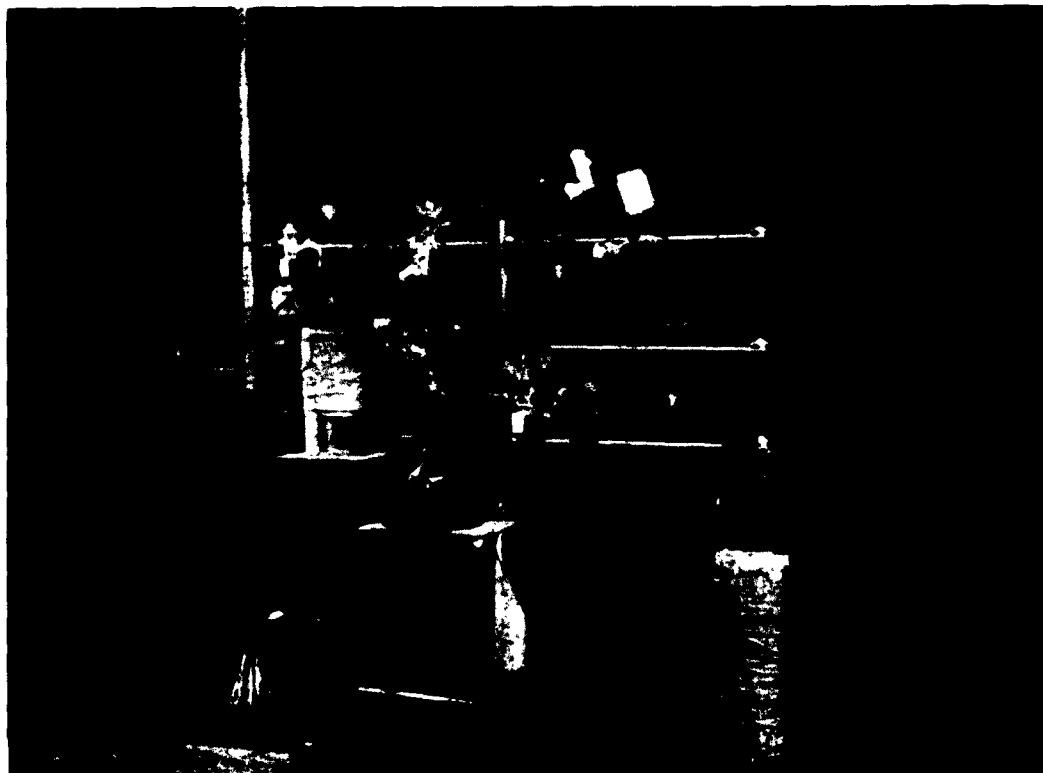
Mass Spectrometer

FIG 19 - APPARATUS FOR HYDROGEN ANALYSIS

Labels in figure: Deuterium, A, B, Liquid Nitrogen Trap, C, D, E, F, H, G, Sample Tube, 37.52 cc Pipet, I, J, Air, Vacuum, Mercury Reservoir, Capillary Manometer

II. PROCEDURE

A. Sampling

Assemble the sampling apparatus (Fig 18) according to the standard sampling procedure. Attach a hydrogen sample reaction tube to the sampling apparatus and lower the nickel bucket into the tube. Place the tube in a furnace at 460°C and degas the bucket by evacuating the assembly. After 1/2 hour, pull the nickel bucket up into the sampling apparatus and close the 15 mm stopcock.

Extract the sample and transfer to the hydrogen sample tube by the standard liquid metal sampling procedure.

Place the sample tube on the hydrogen apparatus (Fig 19) and evacuate the system. Open stopcock F and evacuate the sample tube. Place a liquid nitrogen bath at trap B and admit deuterium in excess of 200 mm to bulb D through stopcock E. Adjust the pressure to exactly 200 mm by evacuating through stopcock C. When pressure is adjusted, turn stopcock E and expand the deuterium into the sample tube. Open stopcock J and I slowly and force the mercury from the reservoir up through the bulk to stopcock F. Close F and return mercury to the reservoir by evacuating through stopcock J. Place sample tube in the furnace (460°C) for 5 minutes, remove and cool to room temperature. Flame the condensed film from the sides of the tube and allow to cool. Place the tube on the mass spectrometer and record the spectrum up to mass 44. Determine the blank for each tube and bucket combination by running them through the procedure.

B. Sample Size

After the sample tube gases have been analyzed, attach a source of nitrogen cover gas to the tube side arm and open the stopcock. Remove the sample tube cap and with cover gas flowing out the tube react the sample with methanol. After the reaction subsides, transfer the tube contents to a beaker, add 50 ml water and titrate to phenolphthalein end point with 2.5N HCl.

Sample wt = (ml x 2.5N HCl x meq)

C. Calculations

Determine the sensitivities and patterns for hydrogen SH_2, deuterium SD_2 and hydrogen deuteride SHD. Calculate the H/D ratio and H concentration as follows:

$$H/D = \frac{(2)/SH_2 + 1/2(3)SHD}{1/2(3)/SHD + (4)/SD_2}$$

where (2) = (total output of 2 peak) - (outputs attributed to D_2 and HD patterns)

$$\text{ppm of H} = \frac{[(H/D)_S - (H/D)_b](k)}{\text{sample wt.}}$$

where S = sample ratio
     b = blank ratio
     k = micromole atoms deuterium introduced into the tube
x 1.008 = 468 x 10^{-6}.

APPENDIX D

DETERMINATION OF CARBON AND CARBON COMPOUNDS IN ALKALI METALS

I. INTRODUCTION

A. Summary

An alkali metal sample is hydrolyzed and acidified. The carbon dioxide from carbonate and the acetylene from carbide are condensed and transferred to a mass spectrometer for analysis. The solution is evaporated to dryness and carbon is oxidized to carbon dioxide in oxygen at 600°C. Carbon dioxide from elemental carbon is condensed and analyzed by the mass spectrometer.

B. Reagents

   Cupric oxide
   Ascarite
   Potassium hydroxide solution (10%) - Dissolve 20 g
       in 180 ml of water
   Hydrochloric acid, 10N
   Hydrochloric acid, 0.01N
   Sodium hydroxide, 0.01N
   Carbon dioxide gas

C. Equipment

   Carbon Analysis Apparatus - There are two systems used in the analysis. Fig 20 is a schematic of the sample dissolution carbide and carbonate system and Fig 21 is a schematic of the apparatus used for elemental carbon analysis.

     Helium Supply - High purity

     Nitrogen Supply - Oil pumped

     Oxygen Supply - Welding grade oxygen is purified of hydrocarbons by flowing through hot (900°C) CuO, a potassium hydroxide scrubber, and ascarite. Flow (100 cc/min) and pressure (1 psig) are controlled by a pressure regulator at the cylinder. The purification train is an integral part of the carbon apparatus.

     Heaters - 350 watt open helical cone. For routine analysis of 4 samples a day at least 5 heaters are required.
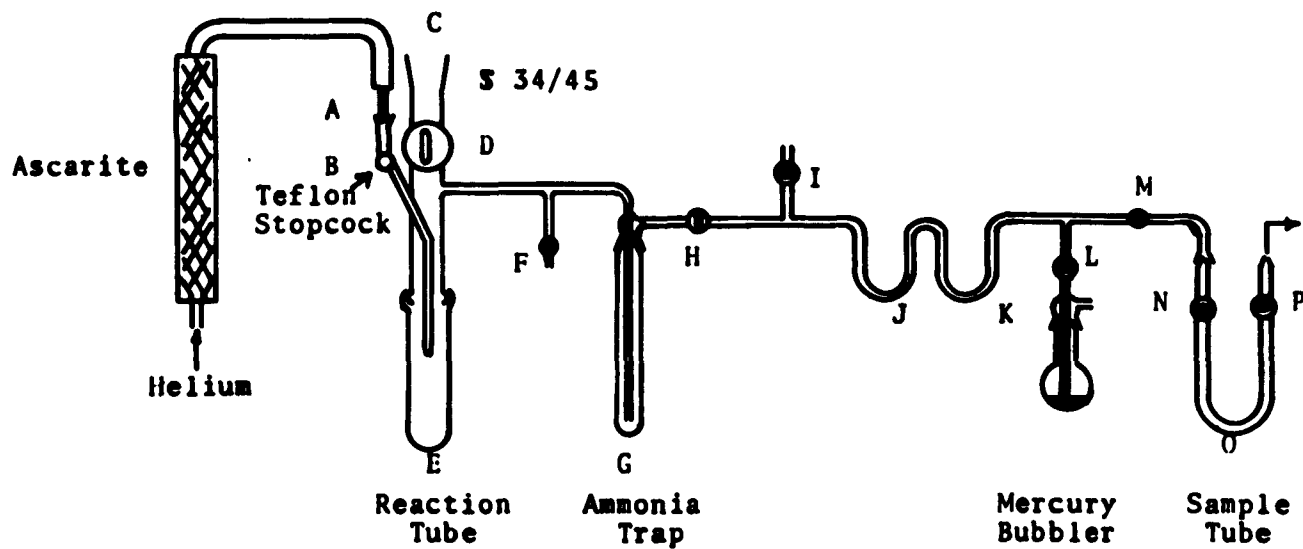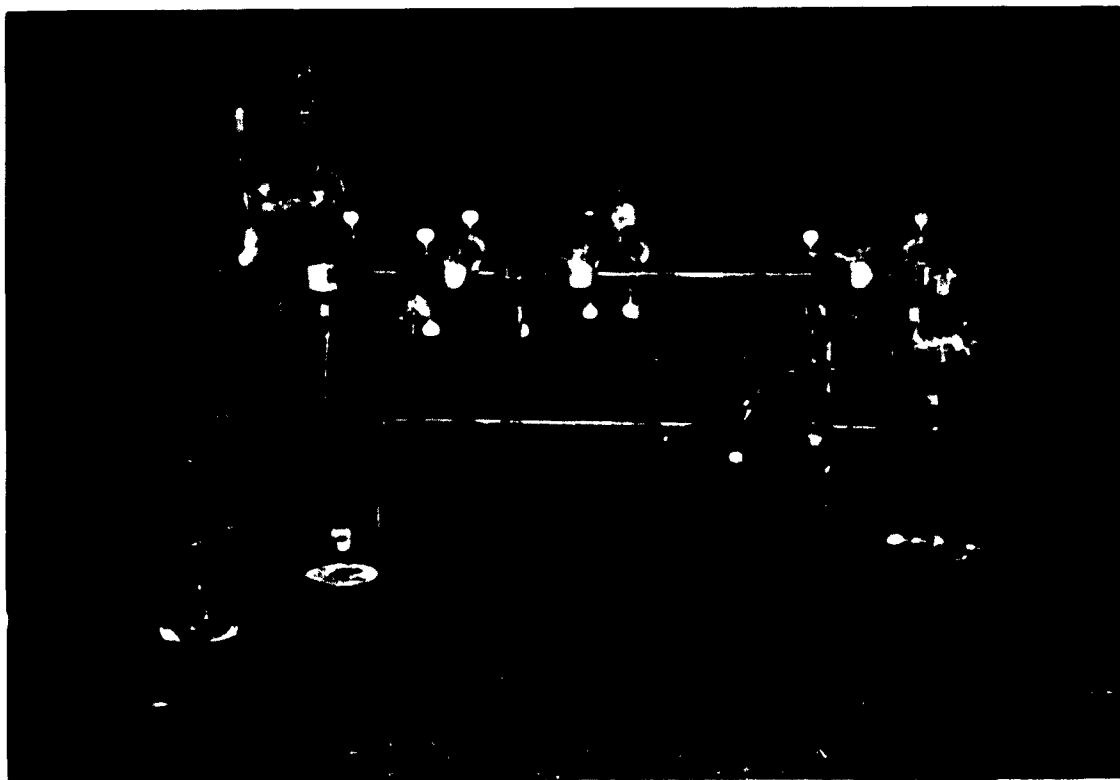
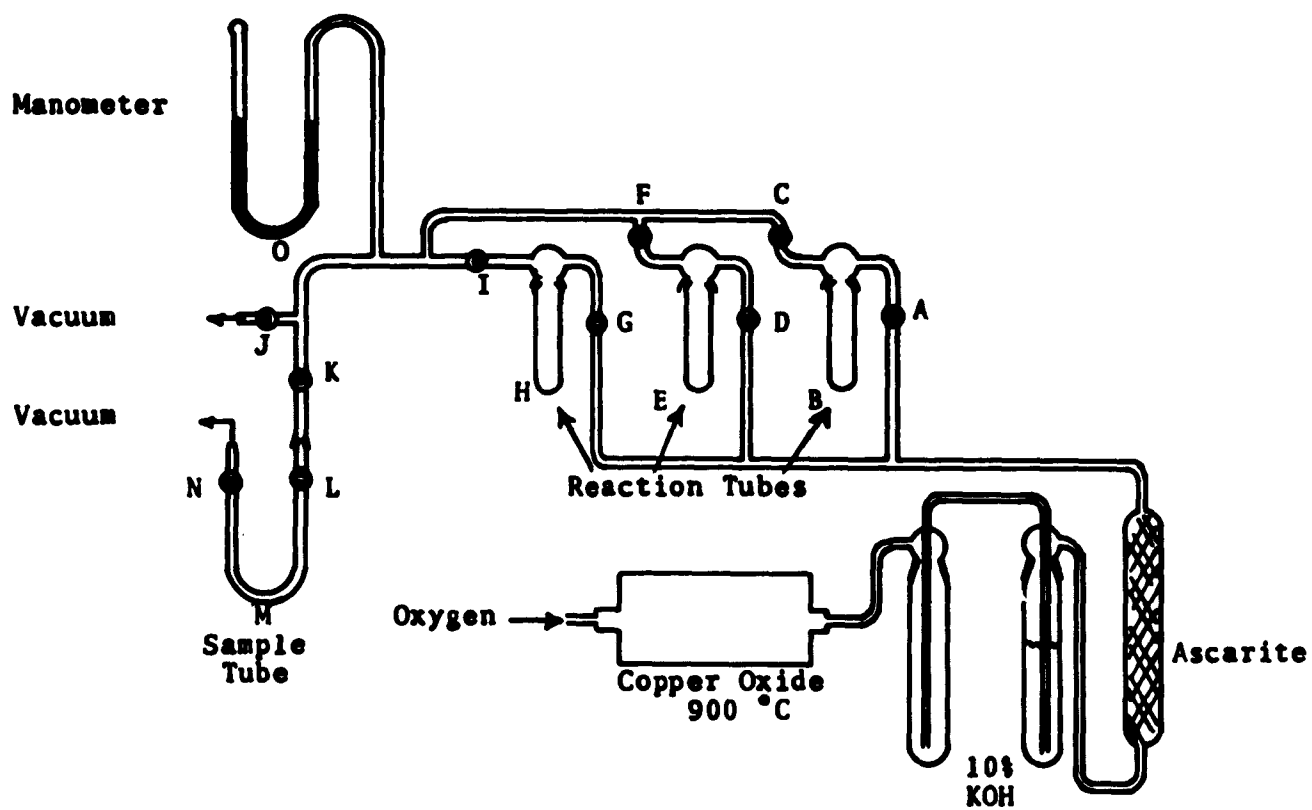FIG 20 - SAMPLE DISSOLUTION AND GAS COLLECTION SYSTEM

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Manometer

Vacuum

Vacuum

Sample
Tube

Reaction Tubes

Oxygen →

Copper Oxide
900 °C

10%
KOH

Ascarite

FIG 21 - CARBON COMBUSTION APPARATUS

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<u>Variable Transformers</u> (5) - One required for each cone heater.

<u>Reaction Tubes</u> - A supply of twelve tubes is required for continuous routine analysis. The tubes are made by sealing off the end of a 35/25 standard socket joint 6 inches from the joint. Etch a line on each tube at the 25 ml level. The tubes are cleaned in hot chromic acid cleaning solution and stored in a drying oven until used.

<u>Burets</u> (2) - Five ml microburet

<u>Syringe</u> - 0.25 ml

<u>Vacuum Pump</u> (2)

<u>Mass Spectrometer</u>

II. PROCEDURE

A. Sampling

Samples are taken from the sampling vessels according to the standard liquid metal sampling procedure.

B. Liquid Metal Dissolution

The sampling apparatus containing the liquid metal sample in a one gram nickel bucket is placed on the dissolution system (Fig 20) at C. Open the 15 mm bore stopcock D, close stopcocks B, I, L. M and evacuate the system through F. Open B and fill with helium to the regulated pressure (1-2 psig) and close B. Open the 15 mm bore stopcock on the sampling apparatus and lower bucket until it rests on the bottom of reaction tube E. Do not touch bucket against sides of apparatus while lowering into tube. Open screw clamp on the dip rod, untwist wire, take one end of nickel wire and pull it through. The sample bucket should be on its side at the tube bottom. Close screw clamp, pull up rod and close stopcock D. Place an ice bath at reaction tube E. Allow 5 minutes for the sample to cool. If a carbonate or carbide analysis is to be done see section on Carbonate Determination before proceeding. Remove helium line from addition tube A, add ten ml of water and replace line. Open stopcock I. to the mercury bubbler vent and add water to the sample one drop at a time through stopcock B. When the reaction is complete, add the remaining water to just cover the sample bucket.

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C. Carbonate and Carbide Determination

Before dissolution of sample by water addition, place a dry ice-acetone bath at trap J and a liquid nitrogen bath at trap K. React the sample with water as described in the preceeding section. After complete dissolution, add 15 ml of 10N hydrochloric acid to funnel A and admit to reaction tube E. Adjust helium flow with stopcock B until a steady flow is maintained through the system. Observe the flow rate by the mercury bubbler. Bring the solution to a boil by gently flaming the reaction tube and allow to cool. Place a liquid nitrogen bath on sample tube O and evacuate to stopcock M. Turn off the helium flow at stopcock B and close stopcocks H and L. The CO_2 and acetylene evolved from the sample are now condensed in trap K. Open stopcock M slowly and pump out the helium in the traps. Close stopcock P and transfer the CO_2 sample tube O by removing the liquid nitrogen bath from trap K. Warm trap K and glass lines slightly with an air dryer. Open stopcock P and pump on the traps for several minutes then close stopcocks N and P. Remove the liquid nitrogen bath from O and transfer sample tube O to the mass spectrometer for carbon dioxide and acetylene analysis at mass 44 and mass 26, respectively.

D. Sample Size

After the sample dissolution or the carbonate procedure, remove the reaction tube from the apparatus, rinse the delivery tube, and fill to the 25 ml mark with distilled water. Take 2 0.02 ml aliquots with a 0.25 ml syringe and place in 2 100 ml beakers. Add 5 ml of water and titrate with 0.01N sodium hydroxide if the carbonate is being determined or with 0.01N hydrochloric acid if only the carbon is being analyzed. Duplicates should agree within 0.1 ml. Calculate sample size from carbonate dissolution as follows:

$$\text{sample wt} = (\text{ml HCl} \times 10N) - (\text{ml NaOH} \times .01N \times \frac{25}{\text{aliquot}}) \times \text{Meq.}$$

For carbon only:

$$\text{sample wt} = \text{ml HCl} \times .01N \times \frac{25}{\text{aliquot}} \times \text{Meq.}$$

E. Carbon Determination

Adjust the solution in the reaction tube to pH 5, place in a cone heater and evaporate to dryness under a nitrogen purge. Control the evaporation by regulating the heater transformer. When

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the solution is evaporated, place the reaction tube on the carbon system (Fig 21). The system has three reaction tubes in parallel so that three samples can be oxidized simultaneously, however, the tubes must be isolated from one another at all times. Evacuate sample trap M and reaction tube H to stopcock G. Close stopcock I and admit oxygen to reaction tube H by opening stopcock G. Close stopcock G when oxygen stops bubbling in KOH scrubber. Place a cone heater on reaction tube H and heat at 600°C for 40 minutes. Remove heater and cool tube with air blower. Place liquid nitrogen bath on sample trap M and reaction tube H and evacuate system through sample trap M to stopcock G. When the manometer indicates all oxygen has been evacuated, close stopcock N and remove nitrogen bath from reaction tube H. Warm reaction tube H and glass line slightly with air blower. Open stopcock N and pump out sample trap M until manometer reads zero. Close stopcock L and N and transfer sample trap M to the mass spectrometer for carbon dioxide analysis at mass 44 peak.

F. Calibration

Determine the sensitivities for carbon dioxide and acetylene on the pure gases at least once a day during routine analysis.

G. Calculations

The volume of each sample trap assembly with the mass spectrometer inlet system must be known. It is only necessary to determine this value once on each sample tube used. This is determined by expanding a known pressure from the sample trap into the mass spectrometer inlet system. Pressure measurements are made with the mass spectrometer inlet manometer. The amount of carbon, and carbonate are determined from the CO_2 condensed in the sample trap assembly from the mass spectrometer data and expressed as ppm carbon and carbonate as follows:

$$nCO_2 = \frac{\frac{(44/SCO_2)}{760}}{RT} (V)$$

where nCO_2 = moles of CO_2 condensed in sample trap
(44) = net output of 44 peak
$S(CO_2)$ = sensitivity of CO_2
V = volume of sample trap in cm^3
R = gas constant 82.057 atmos cm^3
T = ambient temperature in °K

carbon: ppm C $= \dfrac{(nCO_2)(12)}{\text{sample wt.}}$

carbonate: alkali carbonate $= \dfrac{(nCO_2)(\text{carbonate factor})}{\text{sample wt.}}$

The carbide is determined by measuring the acetylene in the sample trap at mass 26 peak:

$$nC_2H_2 = \dfrac{\dfrac{(26)/S(C_2H_2)}{760}}{RT}(V)$$

where nC_2H_2 = moles of acetylene condensed in sample trap
(26) = net output of 26 peak
$S(C_2H_2)$ = sensitivity of acetylene
V = volume of sample trap in cm^3
R = gas constant 82.057 atmos cm^3
T = ambient temperature in $°K$

alkali carbide $= \dfrac{(nC_2H_2)(\text{carbide factor})}{\text{sample wt.}}$

APPENDIX E

DETERMINATION OF NITROGEN IN ALKALI METALS

I. INTRODUCTION

A. Summary

Nitrides in an alkali metal sample are converted to ammonia by reaction with water at 0°C. The ammonia is distilled into an acid solution and analyzed by Nessler Reagent.

B. Reagents

Boric acid (1%) - Dissolve 10 g boric acid in 990 ml of water

Nessler Reagent - Fisher Scientific Co. Remove any sediment by filtration before using

Standard ammonia solution - Dissolve 3.820 g of ammonium chloride in 100 ml water and make up to 1 liter in a volumetric flask. 1 ml = 1.0 mg nitrogen

Hydrochloric acid - 2.5N

C. Equipment

Sample Dissolution and Gas Collection System (Fig 20)

Vacuum Pump

Photometer - Klett-Summerson photometer with No. 42 filter (400-465 mu) or equivalent

Buret - 50 ml

II. PROCEDURE

A. Sampling

Samples are taken from the sampling vessels according to the standard alkali metal sampling procedure.

B. Alkali Metal Hydrolysis and Ammonia Collection

The sampling apparatus containing the alkali metal sample is placed on the dissolution system (Fig 20) at C. Open the 15 mm bore stopcock D, close stopcocks B, I. L, M and evacuate the system through F. Open B and fill with helium to the regulated pressure (1-2 psig). Open the 15 mm bore stopcock on the sampling apparatus and lower bucket until it rests on the bottom of reaction tube E. Do not touch bucket against sides of apparatus while lowering into tube. Open screw clamp on the dip rod, untwist wire, take one end of nickel wire and pull it through. The sample bucket should be on its side at the tube bottom. Close screw clamp, pull up rod and close stopcock D. Place an ice bath at reaction tube E. Remove bubbler G, maintaining a slight helium purge through the bubbler tip, add 50 ml of 1% boric acid and replace the bubbler on the system. Open stopcocks H and L and vent the slow helium purge through the mercury bubbler. After a 5-minute purge, close stopcocks B and L, remove helium line from addition tube A, add 15 ml of ammonia free water and replace line. Open stopcock L to the mercury bubbler vent and add water to the sample one drop at a time through B. For lithium dissolution, water may be added rapidly. When the reaction is complete, add the remaining water and purge slowly with helium. Distill the ammonia into trap G by boiling the solution in reaction tube E for 5 minutes, while maintaining the helium purge. Turn off the helium purge at B and remove trap G. Place 10 ml of the solution from trap G in a 50 ml volumetric flask, add 2 ml of Nessler reagent and make up to volume with ammonia free water. Allow 5 minutes for color development and measure the optical density in a 2 cm cell at 400-465 mu (Filter No. 42 for the Klett-Summerson Photometer) using a reagent blank as a reference solution.

C. Sample Size

Remove reaction tube E, rinse the delivery tube and transfer the solution to a beaker. Titrate to phenolphthalein end point with 2.5N HCl.

$$\text{sample wt} = (\text{ml HCl})(2.5N)(\text{Meq})$$

D. Calibration

Dilute 10 ml of the standard nitrogen stock solution to a liter (0.01 mg nitrogen per ml). Pipett 0.5, 1.0, 2.0, 5.0, 10.0, 15.0, and 20.0 ml of the standard solution into 50 ml volumetric flasks, add 2 ml Nessler Reagent, 10 ml boric acid solution and make up to volume with water. Read after 5 minutes. Prepare a graph relating optical density to nitrogen concentration.

E. Calculation

$$\text{\% Alkali metal nitride} = \frac{(\text{mgN})(\text{aliquot factor})(\text{nitride factor})}{\text{sample wt.}}$$